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Dewatering Of Biosolids By Sodium Ferrate

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DEWATERING OF BIOSOLIDS BY SODIUM FERRATE

by

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ABSTRACT

This study was conducted to evaluate the effectiveness of the liquid form of ferrate for dewatering of biosolids from wastewater treatment facilities. Two different ferrate products prepared using calcium hypochlorite and sodium hypochlorite were used. Samples of anaerobic digested sludge and waste activated sludge with solids content of 2.1% and 0.95 %, respectively were conditioned with both products to evaluate and compare their effectiveness. Centrifugation and filtration of the sludge after conditioning were used. For centrifugation the volume reduction and the turbidity of the supernatant after centrifugation were evaluated. For filtration, the Capillary Suction Time test was used.

The optimum doses and conditions for dewatering of the sludge using ferrate were determined for each type of sludge. The centrifugation and filtration results were compared with those obtained for polymer doses currently used at the wastewater treatment plants where the samples were collected and with ferric coagulants as well.

The results of this research indicated that optimum pH was 7.0. The time required to achieve mechanical equilibrium defined as the time at which the volume occupied by the solids was no more than one percent of the preceding reading was 1800 seconds for both types of sludge. The optimum rotational speeds were 800 and 2400 for waste

activated sludge and anaerobic digested sludge, respectively. The optimum ferrate dose for anaerobic digested sludge for centrifugation and filtration was 5000 mg/l. For waste activated sludge a dose of 10 mg/l was found to be effective for filtration and centrifugation.

The results indicated that the ferrate product prepared using calcium hypochlorite provides better results for the waste activated sludge than the ferrate prepared using sodium hypochlorite, while for anaerobic digested sludge no significant difference was observed. Finally, the results show that ferrate is a cost-effective alternative for the conditioning and disinfection of waste activated sludge, but not for the conditioning of anaerobic digested sludge.

To my mom and my best friend Edith

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1 INTRODUCTION

The implementation of more stringent water-quality standards is expected to result in a rapid and significant increase in the generation of wastewater biosolids, as well as requirements for pathogens destructions in these biosolids. Dewatering and disinfection of the biosolids are two important operations in a wastewater treatment plant and often demand significant capital equipment and operating costs. The efficiency of sludge dewatering and disinfection also has significant impact on disposal options such as land application program.

Ferrate (Iron VI) ion is powerful oxidant and an experimentally proven and effective coagulant and disinfectant for various water and wastewater treatment processes (Gilbert et al. 1976; Lee et al. 2003; Sharma 2002). Previous studies have evaluated the properties of ferrate as coagulant a disinfectant, but no its application as conditioning agent for sludge. Prior synthesis methods for the production of ferrate made it extremely expensive, and its use for big scale applications was never considered.

Ferrate Treatment Technologies, LLC has developed a novel synthesis method for the onsite production of the liquid ferrate based on the wet oxidation method (Thompson et al. 1951; White and Franklin 1998) consisting of the oxidation of ferric ion using hypochlorite in a strong alkaline solution. This technology reduces the cost of ferrate production, making it commercially feasible. Prior to commercialization efficacy and

dose requirement for different applications have to be determined. This study evaluates the effectiveness and dosage requirements of this liquid product for the dewatering of biosolids, as well as the optimum conditions for filtration and centrifugation when ferrate is used. A review of the existing literature on properties of the sludge, types of sludge, conditioning agents for sludge, chemistry of ferrate and applications of ferrate is presented in Chapter 2. Chapter 3 provides a description of the methodology used to conduct this study. The results and discussion for the study are presented in Chapter 4, and the conclusions and recommendations are presented in Chapter 5.

2 LITERATURE REVIEW

2.1 Introduction

The biological treatment of municipal or industrial wastewater results in the production of a semisolid waste material known as biosolids. The implementation of more stringent water-quality standards is expected to result in a rapid and significant increase in the generation of wastewater sludge (Mc Farland 2000). It has been reported that the costs related to sludge dewatering alone may be as high as 30 to 50% of the total annual operation cost for a wastewater treatment plant. Therefore, much more attention has been paid during the last decade to all sludge handling processes (Mc Farland 2000; Neyens et al. 2003). Dewatering of the sludge is an important operation for the handling the sludge, which reduces the moisture content of the sludge facilitating its final disposal. Dewatering is usually accompanied by chemical or physical conditioning processes which improve the water removal by enhancing properties such as coagulation and flocculation of the sludge.

This chapter provides a review of the literature on the biological, chemical and physical properties of the sludge, classification of the sludges, and sludge conditioning and dewatering techniques. The chemistry of ferrate, its effects in previous research, and

its potential applications for wastewater and sludge treatment are briefly discussed, as well.

2.2 Wastewater Sludges

Wastewater sludges are semisolid odiferous residuals generated from the treatment of wastewaters and consisting of particles aggregated into flocs that act hydro-dynamically as single particles. These flocs can be found in suspension without touching other flocs (e.g. chemical sludge in water treatment prior to settling) or in a solid matrix where individual flocs cannot be identified and the sludge mass forms a continuum. (Gurjar 2001; Sanin and Vesilind 1994). In general, untreated sludges have offensive odors, and contain a large number of pathogens microorganisms. However, when treated, sludges can be used as a low-cost alternative to chemical fertilizers due to their nutrient content, specially, nitrogen and phosphorous (Albertson et al. 1991; Mc Farland 2001; Spellman 1997).

There are several sources of wastewater sludges; thus, they are classified according to the treatment stage from which they originate from. In general, wastewater sludges are classified as primary, secondary, chemical or digested sludges. The quality and quantity of these sludges depends on the characteristics of the wastewater that is treated (i.e. solids content, organic and inorganic materials, chemicals used, etc.), the extent of the wastewater treatment, and the expected removals by specific treatment processes. Since wastewater influent is not constant in character nor quality from place to

place nor time to time, the biosolids resulting from its treatment would expected to vary as well (Mc Farland 2001).

2.2.1 Properties of Sludges

As discussed previously, the properties of wastewater sludges vary with respect to time and location, therefore the different forms of produced sludge contain different constituents. However, the major common component is water, which may be up to 95% by weight of the material. The remaining dry solids contain variable proportions of nitrogen, phosphorous, potassium, heavy metals, pathogens and other inorganic and organic materials depending on the source of sludge and type of treatment (Albertson et al. 1991; Mc Farland 2001; Shien et al. 1988). This section summarizes the physical, chemical, biological, and biochemical properties of sludge that are commonly used for its characterization and evaluation of dewatering properties.

2.2.1.1 Physical Properties

The physical properties of the sludge pertain to the physical nature of the sludge and determine, to a great extent, the possibilities and conditions that can be use for the treatment (i.e. conditioning, stabilization, etc.) and disposal of the sludge. The most important physical properties are given below

Specific Gravity is defined as the ratio of the weight of the material to that of an equal volume of water. Most sludges have a specific gravity varying between 0.95 and

1.03 (Gurjar 2001; Mc Farland 2001;Vesilind 1979). This property depends on the nature and proportions of fixed and volatile solids and the water content of the sludge. In general, sludges are composed of only one solid and one liquid, thus the specific gravity must be calculated as (Vesilind 1979).

$$1/S_s = \sum_{i=1}^{n} (W_i / S_i) \tag{2.1}$$

Where:

S_s = Specific gravity of the sludge (dimensionless),

W_i = Weight fraction of the i^{th} component of the sludge (dimensionless),

S_i = Specific gravity of the i^{th} component (dimensionless).

Solids content is the relative concentration of a solid fraction of a sludge expressed as mg/l or percent solids (expressed in terms of weight/weight). The total solids in a sludge represent the material residue left in a vessel after evaporation of a sample and its subsequent drying in a oven at a defined temperature (generally, 105 °C) to its complete dryness. The percent solids can be calculated using Equation 2.2.

$$\%Solids = \frac{W_r}{W_s} * 100 \tag{2.2}$$

Where:

W_r = Weight of dried residue (mass),

W_s = Weight of the initial sample before it is dried at 105 °C (mass)

Settling is a function of the total solids present in the sludge and may be used as an indicator of the retention time required for sedimentation tanks or clarifiers. It is also used to determine the volume that will be occupied by the solids when they settle. The settling rate for a specific sludge depends on how easily the solids can move to the bottom of the settling unit, and their ability to displace an equal volume of water to the top of the unit. This water finds its way to the top of the settling unit more easily if a great many void spaces exist between the sludge solids; therefore dilute sludges settle faster and more concentrated sludges settle slower (Vesilind 1979).

Electrical Charge is a fundamental property of the solid particles in the sludge, which determines their electromagnetic interactions. In general, sludge solids have a negative surface charge and therefore repel one another (Gurjar 201; Mc Farland 2001). As a result, sludge particles will attract positively charged ions (cations) from the water solution to counter balance their negative charge. This phenomenon is called the diffuse double layer theory.

Particle Size of sludges varies with time not only in magnitude but also consistency and shape. Therefore, it is extremely difficult to characterize sludges by this singular property. (Vesilind 1979). However, it has been categorized by several researchers (Guan and Waite 2003; Langer et al. 1994; Nellenshulte and Kyser 1997;

Vesilind 1979) as the most important parameter affecting the dewatering behavior of sludges. The importance of particle size distribution in dewatering operations results from its influence on the variation of specific surface area of the sludge, and the effect that it can cause on the increase of total electrical charge for the sludge. As the average size decreases, the surface area for a given sludge mass increases. Thus, factors affecting removal of water such as more electrical repulsion between particles, higher frictional resistance to water movement, and more available sites for adsorption of water are observed (Shin et al. 1988; Nellenshulte and Kyser 1997).

Water Content is one of the most important parameters used to control and operate sludge processing operations, given that it occupies the largest portion of the sludge and determines to what extent the total volume of sludge can be reduced during dewatering operations. Water is distributed within the sludge in several different forms and that each of these forms behaves different. Therefore, it is very important to know the characteristics and behavior of this water to evaluate the performance of dewatering mechanisms and operations.

Vesilind and Martel (1990) stated that water exists in several easily identifiable forms including: free water, interstitial water, surface water and bound water within the sludge and defined them as follows:

- *Free water* is the fraction of water that is not associated with solid particles. This water surrounds the sludge flocs, but does not move with them. This water includes void water that is not affected by capillary force.
- *Interstitial water* is the water that is trapped within the flocs, travels with the floc and is

held by capillary forces between the particles. This type of water can be removed by mechanical devices that compress the flocs and expel the water.

- *Surface water* is water held on the surface of solid particles by adsorption and adhesion forces. It is also called vicinal water.
- *Bound water* is the fraction of water that is chemically bound to the solid particles.

Figure 2.1 depicts the distribution of these types of water within the sludge.

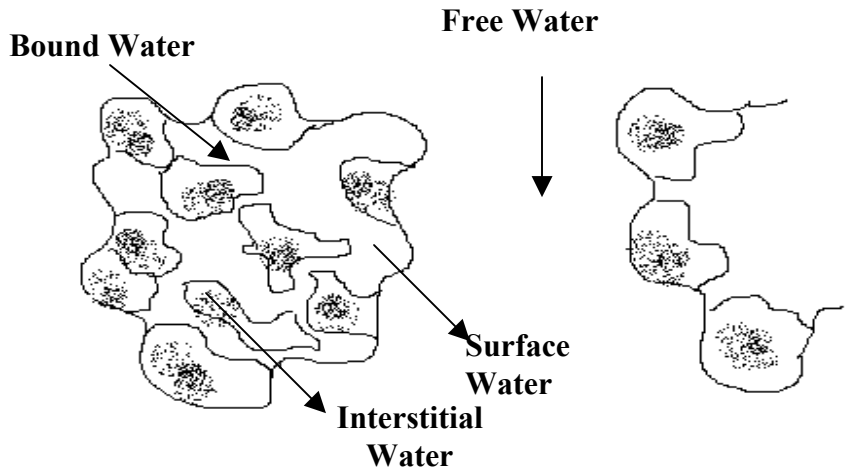


Figure 2.1 Water Distribution in Sludge. (Source: Gurjar 2001)

Rheology is mainly defined by two properties, yield strength and viscosity. Rheology describes the stress necessary to produce significant deformation in the sludge under compressive load, and the resistance to flow, respectively. These properties vary from sludge to sludge and are a function of temperature and solids concentration (Vesilind 1979). As the solids concentration increases, the yield strength and the

viscosity become greater and a higher stress is necessary for the water to find its way out of the sludge matrix. Temperature on the other hand reduces the viscosity of the sludge as it increases, and therefore enhances the flow of the water. Typical sludge rheological properties are presented in Table 2.1.

Table 2.1 Typical Sludge Rheological Properties

Sludge	Temperature (°C)	Solids (%)	Yield Strength (dynes/cm^2)	Viscosity (g/cm-sec)
Raw Primary	12	6.7	43	0.28
Activated	20	0.4	0.1	0.06
Mixed Digested	17	10	15	0.92

Source: Shin et al.1988.

2.2.1.2 Chemical Properties

The chemical properties of the sludge describe its potential to undergo some chemical change or reaction by virtue of its composition. Thus, they are significant parameters required to define the performance of stabilization operations (treatment of the sludge to achieve reduction of pathogens concentration and elimination of offensive odors). Some chemical properties of the sludge are described below.

Fuel value is the amount of energy that can be produced from the sludge. This property is a function of the volatile or total organic dry solids contained in the sludge

and can be expressed empirically as in Equation 2.3 (Gurjar 2001).

$$Q = a[P_v - b\ ][100 - P_c\ ]/[(100 - P_c\ )*100\ ] \qquad (2.3)$$

Where:

Q = The fuel value of the solids/sludge (BTUs (British Thermal Units) per pound dry weight).

P_v = Proportion of volatile matter (%)

P_c = Proportion of chemical, precipitating or conditioning reagent (%)

a,b* = Coefficients for different classes of waste solids/sludges for plain sedimentation municipal wastewater sludges (fresh and digested) a= 131, b= 10, while for fresh activated sludge a= 107, b=5, Gurjar 2001.

Fertilizer Value refers to the content of nutrients such as nitrogen, phosphorous (as P_2O_5) and potassium (as K_2O) in the sludge, which make it suitable as a fertilizer. Most of the sludges from wastewater treatment contain high percentages of these nutrients, therefore their reuse under appropriate conditions for land applications is commonly used. Some typical nutrient concentration values for different types of sludges are presented in Table 2.2.

Table 2.2 Typical Nutrient Concentrations of Municipal Wastewater Sludges

Sludge	%Nitrogen (N)	% Phosphorous (P_2O_5)	%Potassium (K_2O)
Raw Primary	2.9	1.6	-
Trickling Filter	3.0	3.0	0.5
Activated	5.6	5.7	0.4
Mixed Digested	4.6	1.4	0.38

Source: Shin et al. 1988.

pH value and alkalinity represent the acid or basic composition of the sludge. These parameters are used in process control to determine the performance of operations such as digestion and activated sludge. These factors are also important because they determine the interaction of the conditioner agent with the surface of the sludge colloids (Shin et al. 1988; Tixier et al. 2003).

2.2.1.3 Biological Properties

Several researches have defined taxonomy (the classification of organisms) and the presence of pathogenic organism as the two main biological characteristics of interest for sludges (Gurjar 2001; Shin et al. 1988; Vesilind 1979). The types of organisms present in the sludge change continually and mostly depend on the substrate and ambient conditions. In general, primary sludge contains a tremendous variety of organisms from human intestinal tract and other sources. Secondary biosolids such as activated sludge

which have not gone through stabilization contain bacteria, molds, rotifers, yeast, protozoa, and crustaceans. The pathogens that are generally present in wastewater sludges are fecal coliform, enteric viruses, Salmonella sp, Ascaris, and Viable helminth ova (Mc Farland 2001).

2.2.1.4 Biochemical Properties

The biochemical properties of the sludge refer to the chemical composition of a particular living system or biological substance present in the sludge. Some researchers who have studied these properties have established four as the most important biochemical properties for sludges;(1) Adenosine Triphospate (ATP), (2) Dioxyribonucleic acid (DNA), (3) enzymes, and (4) extracellular Polymers (ECP) and Extracellular polysaccharides (EPS). These materials act as a protective barriers to the living microorganisms, keep them attached to the floc and give the floc its integrity and rigidity (Houghton and Stephenson 2002; Neyens et al. 2004; Sanin and Vesilind 1994).

Sanin and Vesilind (1994) investigated the composition of activated sludge systems and suggested that ECPs and EPS were the main components of those types of sludges after cells and water.

2.2.2 Classification of the Sludges

Wastewater sludges may be classified on the basis of their composition or according to the treatment stage from which they originate. The characteristics of

different types of sludge that are generally produced in wastewater treatment are presented in this section.

2.2.2.1 Primary Sludge

This type of sludge is produced from primary settling tanks. It is gray, sticky, has an obnoxious odor, and does not drain freely. It can be air dried only in thin layers and the supernatant (water from sludge) is turbid and smelly (Gurjar 2001).

2.2.2.2 Chemical Sludge

Chemical sludges result from chemical treatment processes, and are not biologically active. This type of sludge is usually dark in color, has an obnoxious odor but not as strong as primary sludge. It gives off gas in substantial quantities and its density increases when allowed it to stand.

2.2.2.3 Trickling Filter Sludge

This type of sludge is produced from low-rate biological filters, which are used as part of the wastewater treatment system to degrade organic mater. It is brownish in color, flocculent and contains many dead worms, which produce offensive odors. The trickling-filter sludge does not drain readily and is usually digested prior to dewatering to improve its drainability.

2.2.2.4 Activated Sludge

Activated Sludge is a flocculated suspension of living and dead microorganisms, organic and inorganic matter held together in polymer matrix formed by exocellular biopolymers and cations. In this type of sludge, most of the biopolymer is incorporated into the activated sludge matrix, but a portion of it remains unattached in solution as biocolloids which are negatively charged (Novak et al. 2003). This type of sludge has poor drainability, is golden-brown in color and has earthy odor. If the color is lighter than usual, the sludge may have been under aeration for a time longer than needed, with a tendency for the solids to settle slowly. If the color is quite dark, it may be approaching a septic condition (Gurjar 2001).

2.2.2.5 Aerobic Digested Sludge

In aerobic digestion, sludge is biochemically oxidized by aerobic bacteria in an open or closed vessel. To supply these aerobic microorganisms with enough oxygen to carry out their task, the sludge must be agitated by a mixer or injected with air. Under aerobic conditions, the volatile solids in the sludge are converted to carbon dioxide, water and nitrates (USEPA 1999). This type of sludge is brown to dark brown in color, is flocculated, and its odor is not offensive. Aerobic digested sludges have appreciable fertilizer value and high drainability (Mc Farland 2001).

2.2.2.6 Anaerobic Digested Sludge

Anaerobic digestion is a biological process that uses bacteria that function in an oxygen-free environment. These bacteria convert volatile solids into carbon dioxide, methane, and ammonia. The reaction takes place in a closed tank that may or may not be heated. There are basically two types of anaerobic digestion systems, standard rate and high rate. Standard-rate systems take place in a simple storage tank with sludge added intermittently. The only agitation that occurs comes from the natural mixing caused by gases rising to the surface. Standard-rate operations can be carried out at ambient temperatures, although heat is sometimes added to speed up the biological activity. The high-rate systems use a combination of active mixing and carefully controlled, elevated temperatures to increase sludge stabilization (USEPA 1999). This type of sludge is dark brown to black in color, contains a large quantity of gas, and its odor is relatively faint. Anaerobic digested sludges are not offensive when thoroughly digested, and can be used directly as fertilizers.

2.2.2.7 Septage

Septage sludge comes from septic tanks, which are tanks used to manage domestic wastes when a sewer line is not available to carry them to a treatment plant; frequently part of a rural on-site sewage treatment system. This type of sludge is black in color and it is offensive because of the hydrogen sulfide and other gases it gives off (Gurjar 2001).

2.3 Sludge Conditioning and Dewatering

Sludge dewatering is a wastewater treatment process consisting of the removal of water from the sludge to achieve an overall volume reduction and produce a sludge that is no longer a fluid and can be transported in a solid form. Therefore, dewatering is considered one of the most important components of wastewater treatment because it not only reduces the volume of sludge that has to be handle, but also the cost of transportation to the final disposal location. In general, the removal of water from the sludge can be achieved using mechanical or thermal assistance in processes such as centrifugation or vacuum and pressure application, what may increase the dewatering rate and the amount of water that is removed from the sludge. However, the best performance of a dewatering process is achieved when conditioning of the sludge to enhance water removal is provided and combined with mechanical treatment. Mikkelsen and Keiding (2002) defined the optimum sludge dewatering system as one that can achieve a low sludge mass for disposal, a high dry matter content of the dewatered sludge, and a high dewatering rate using a low conditioner dose.

2.3.1 Sludge Conditioning

Conditioning is a process whereby the sludge is treated by chemical or physical means to prepare it for dewatering operations by enhancing water removal and improving solids capture. Several researchers have established that a conditioning process consists of two main steps; coagulation and flocculation (Hogg 2000; Langeret al. 1994; Mc

Farland 2001; Novak et al.1999; Shin et al. 1988). Sludge particles on the sludge are negatively charged and therefore they repel each other due to electrostatic forces. Coagulation involves the destabilization of sludge particles by eliminating interparticle repulsion; flocculation refers to the agglomeration of destabilized particles by collisions that are produced by hydraulic shear (Novak et. al 1999). The conditioning of the sludge can be achieved by chemical or physical methods.

Chemical conditioning involves the addition of organic or inorganic chemicals to facilitate water removal. The addition of inorganic chemicals results in the formation of positive charge particles, which neutralize the negatively charged particles in the sludge. The most common inorganic chemical used is ferric chloride, which forms positively iron complexes that neutralize the negative particles and also form $Fe(OH)_3$, which acts to flocculate the destabilized sludge. The sequence of chemical reactions for the formation of complexes is described by Equation 2.4 to Equation 2.8 (Shin et al. 1988).

$$Fe^{3+} + 6H_2O \longrightarrow Fe(H_2O)_6^{3+} \quad (2.4)$$

$$Fe(H_2O)_6^{3+} + H_2O \longrightarrow Fe(H_2O)_5OH^{2+} + H_3O^+ \quad (2.5)$$

$$Fe(H_2O)_5OH^{2+} + H_2O \longrightarrow Fe(H_2O)_4(OH)_2^+ + H_3O^+ \quad (2.6)$$

$$Fe(H_2O)_4(OH)_2^+ + H_2O \longrightarrow Fe(H_2O)_3(OH)_{3(s)} + H_3O^+ \quad (2.7)$$

$$Fe(H_2O)_3(OH)_{3(s)} + H_2O \longrightarrow Fe(H_2O)_2(OH)_4^- + H_3O^+ \quad (2.8)$$

The formation of these complexes depends on pH. They are generally formed in significant amounts in sludges with pH between 4 and 7 (Shin 1988). In some cases, ferric chloride is used in conjunction with lime, which reacts with the alkalinity present on the sludge to form calcium carbonate as shown in Equation 2.9. The formed calcium carbonate increases the porosity of the sludge and reduces its compressibility (Mc Farland 2001).

$$Ca(OH)_2 + Ca(HCO_3)_2 \longrightarrow 2CaCO_3 + 2H_2O \quad (2.9)$$

Some other chemicals that are commonly used to condition sludge are organic polymers, which are large molecules consisting of repeated chemical units joined together in chains, and containing ionized groups. The segments of the chain containing these groups form interparticle bridges between the sludge particles, and in this way large flocs are formed. Depending on whether they are positively, negatively or neutrally charged, polymers are categorized cationic, anionic or nonionic (Langer et. al 1994; Novak et. al 1999). In general, chemical conditioning provides cakes with a solids content ranging from 15 to 20 %.

Thermal conditioning is a physical process consisting of the heating of sludge at temperatures ranging from 200 to 400 °F. This process promotes the breakdown of biological sludge cells and the release of the water that is bound within the cell structure. This process offers different advantages for sludge treatment operations given that it not

only enhances water removal from the sludge, but also increases the dewatering rates by reducing the viscosity of the water due to the high temperatures. It acts as an effective sludge stabilization process providing disinfection of the sludge and produces a more readily dewaterable sludge (solids contents of 30 to 40%) than that one obtained with chemical treatment (Lin and Shien 2001; Mc Farland 2001; Shin 1988). However, this treatment promotes not only the release of water but the release of bound organic material that is inside the cells, which results in the increase of soluble dissolved oxygen consumption in five days by biological processes breaking down organic matter or Biochemical Oxygen Demand (BOD_5). The presence of BOD creates a separate problem related to this side stream.

The most common thermal conditioning treatments currently employed for pretreatment of sludge are wet air oxidation and heat treatment of sludge. Both systems operate based on the same principle. However, the wet oxidation process introduces air into the conditioning system providing some oxidation of the organic material whereas the heat treatment process does not (Mc Farland 2001).

Novak et al. 1988 showed that floc formation when polymer was used for the conditioning of the sludge occurs in three steps; (1) addition of polymer, (2) rapid mix to break the bioflocs and achieve complete contact between the sludge and the polymer, and (3) slow mixing for the agglomeration of the formed flocs.

Whenever conditioning is used for the pretreatment of sludge prior to dewatering, different chemical and physical transformations take place which are influenced by the characteristic of the sludge or the conditions at which the conditioning process is carried

out. Therefore, the characteristics of the sludge and conditions prior to conditioning have to be evaluated to predict the needed treatment and dosages, as well as to predict the performance of the selected conditioning system.

Researchers who have evaluated the impact of different parameters on conditioning processes have established that the most important factors affecting the conditioning process are particle size, temperature, pH, amount of colloidal particles, ECPs and mixing conditions (Liao et al. 2000; Mikkeisen and Keiding 2001; Nellenschulte and Kayser 1997; Tixier et al. 2003).

Particle size has a significant impact on the required dose for the conditioning of the sludge given that it defines the surface area that will be negatively charged and has to be destabilized during the conditioning process. Also, size impacts the amount of water that will be retained on the surface due to adsorption or capillary action. The smaller the particles, the greater the negatively charged surface area for a given sludge mass, and therefore the amount of conditioner that is required for pre-treatment before dewatering.

Tixier et al.(2003) conducted a study on different types of sludge using different pH conditions, and observed that there is an isoelectric point (pH of a solution in which protein has no net charge) for bacteria and colloidal particles between pH 2.0 and 4.0. They also reported that the sludge particle surfaces would carry increasingly negative charges as the pH is increased above the isoelectric point. Thus, pH is an important factor for the conditioning of the sludge because it determines the surface charge on the sludge and therefore the amount of conditioner that would be needed for the complete stabilization of this resultant charge.

Studies conducted for different types of sludge indicated that the presence of ECPs on the sludge affects the conditioning and dewatering properties of the sludge (Liao et al. 2000; Mikkeisen and Keiding 2001; Nellenschulte and Kayser 1997). As mentioned before, ECPs are organic polymers produced by bacterial cells that are present in the sludge matrix, and may contain amounts of water up to 99 % by weight, and therefore retain a high level of water in the sludge. When these biopolymers bind cells and particle matter together, they also change the particle size distribution and therefore, alter the coagulation process. Investigations on the effect of these biopolymers within the sludge indicated that their presence in the sludge has a negative influence on the hydrophobicity and surface charge of the particles. Therefore they have a negative impact on conditioning processes, given that they increase the amount of water in the sludge, especially bound water, change the size distribution and increase the negative surface area (Liao et al. 2000).

Mixing is another factor critical to sludge conditioning. This parameter is important because it affects the mechanisms of floc formation in sludge conditioning. In general, the mixing has three components; sequence of chemical addition, and intensity and duration of mixing (Shin et al. 1988). It has been shown that during conditioning of sludge the flocs are formed immediately after dispersion of the chemical conditioner, and that this phenomenon occurs within seconds, while the flocculation of the formed flocs occurs within one to three minutes (Langer et al. 1994; Novak et al. 1988; Shin et al. 1988). Consequently, a short duration of high mixing is needed for complete dispersion of the added conditioner and slow but longer mixing is needed for the flocculation step to

achieve complete agglomeration of the flocs preventing the breakage of the formed flocs. The optimum mixing conditions will depend on the viscosity of the conditioner and the sludge, which will determine the needed mixing intensity and the time needed for flocculation. If mixing conditions are underestimated, a high risk of incomplete contact between conditioner and sludge may occur, and if mixing is exceeded it can cause breakage of the flocs that are already formed.

The methods that are commonly used for the evaluation of conditioning aids are mainly divided into two categories; laboratory scale tests, and bench and pilot-scale tests which are conducted for specific dewatering unit processes. Laboratory scale tests are the Buchner funnel test for the determination of resistance to filtration, the Capillary Suction Time (CST) test for preliminary screening aids on filtration processes, and standard jar tests (Grujar 2001; Mc Farland 2001; Shin et al. 1988).

The bench and pilot-scale tests are divided into (1) centrifugation to evaluate the effect of centrifugal force in dewatering systems, retention times, and required doses and (2) the floc strength test to measure the rate of sludge compaction, and (3) strobe light techniques.

2.3.2 Mechanisms of Dewatering

As discussed previously, four types of water are present within the sludge; free water, interstitial water, surface water, and bound water, and each of them can have an important role defining the dewatering characteristics of the sludge. After the sludge is

conditioned by chemical or physical methods the water can be readily removed during dewatering operations using mechanical or heating methods. The behavior of a molecule of water during the dewatering process is dependent on its proximity to the solid. In general, two types of water are considered to have the biggest impact on the dewatering processes; the free water and the bound water. Free water is the water that can be removed from the sludge, and bound water is the portion that remains inside the flocs.

The free water is the easiest fraction of water to be removed given that it is not influenced by solid particles. This fraction of water can be eliminated prior to conditioning by mechanical means such as drainage or gravity thickening. Some researchers suggest that this fraction of water increases when the water molecules absorbed by the solid particles (surface water) can be converted into free water when chemical conditioners are added to the sludge. They are released as free water by their replacement by chemical molecules or by the destruction of the binding capacity to the particle (Colin and Gazbar 1995; Katsiris 1987;Vaxelaire 2004).

The interstitial water which is trapped inside interstitial spaces or flocs and organisms can only be released by the destruction of the floc structures or by using of enough mechanical energy to squeeze the water out. In general, the free and interstitial water can be removed by mechanical methods.

Two fractions of water that can not be removed by mechanical mechanisms are the surface water and the bound water. The surface water which is it attached to the solids by adsorption and capillary forces requires chemical conditioning to be released from the surface and then can be removed by mechanical means. The bound water

however, is chemically bound to the solids and is not available for dewatering even with conditioning (Vesilind 1989). Researchers who studied the properties of this type of water established that even though this fraction of water is small compared to all the water on the sludge, it has a large effect on the sludge dewaterability since it prevents many small particles from coming into contact and adhering to one another during mechanical operations (Vesilind 1989; Vexalaire and Cezac 2004).

Vesilind (1990) also established that this water can be removed from the sludge by using heat energy and evaporation, which will enhance the removal of a large amount of free water by altering the characteristics of the sludge particles, creating more void spaces.

2.4 Ferrate: Iron (VI)

2.4.1 Introduction

Ferrate (Iron VI) ion is a very powerful oxidant and an experimentally proven and effective coagulant and disinfectant for various water and wastewater treatment processes at very low doses (Gilbert et al. 1976; Sharma et al. 2004). Ferrate therefore has been considered as a suitable reagent to be used in wastewater applications. Due to its properties as an effective coagulant and disinfectant, ferrate can be a potential coagulant agent for the conditioning of the sludge prior to dewatering.

2.4.2 Ferrate Chemistry

Ferrate has the molecular formula FeO_4^{-2} in which iron has an oxidation state of +6. It is a powerful oxidant over the entire pH range. It possesses properties such as high functional group selectivity, high oxidizing power (which varies from 2.2 V to 0.7V in acidic and basic solutions, respectively) and non-toxic decomposition by-products, primarily the ferric ion. Ferrate is an environmentally-friendly oxidant which can oxidize a large number of organic and inorganic pollutants in aquatic environments, substituting for oxidants of environmental concern such as chlorine and chromate (Sharma 2002).

Several researchers who have studied the chemistry of ferrate agree that ferrate has a tetrahedral structure in which four equivalent oxygen atoms are covalently bonded to a central iron atom in +6 oxidation state (Goof and Murman 1971; Lee et al. 2003; Rush et al. 1989). Norcross et al. (1997) proposed that ferrate can have three resonance hybrid structures in aqueous solution as shown in Figure 2.2.

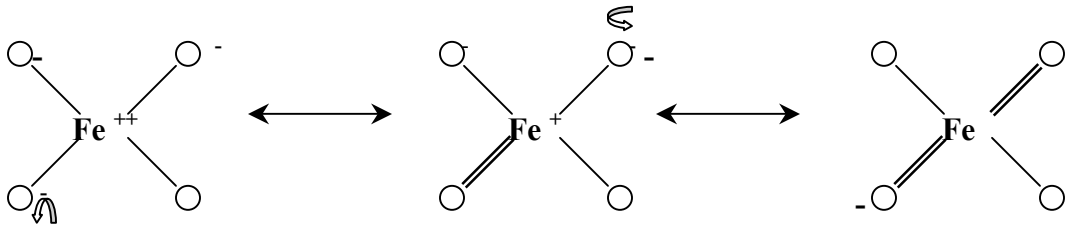


Figure 2.2 Three Resonance Hybrid structures of Fe (VI) Ion in an Aqueous Solution. (Adapted from Lee et al. 2003)

Wagner et al. (1952) evaluated the effects of alkalinity, temperature, and concentration on the stability of potassium ferrate. They conducted studies using 0.010M solutions of potassium ferrate in different molar concentrations of sodium hydroxide varying from 3 M to 6M, and observed that the ferrate solution presented lower decomposition to ferric ion in higher concentrations of caustic solution. Temperature effect was evaluated by reducing the temperature to -20°C after preparation, and it was observed that the complete decomposition of ferrate occurred within seven days at room temperature, while just 29.3% decomposition occurred after 31 days for the cold sample indicating that low temperatures provide higher stability for the product. The concentration effect was evaluated by analyzing the decomposition of various solutions with different molar concentrations of ferrate over time. Low iron concentrations offered more stability. These results clearly indicated that alkalinity, temperature and concentration have significant impact on the stability of ferrate solutions. Rush et al.(1989) also indicated during the study of reduction of Fe(VI) to Fe(V) that the decomposition of ferrate is lower at low iron concentrations and more stable at pH values above 9.0.

Ferrate has a characteristic purple color in aqueous solution and visible absorbance spectra which has maximum absorbance at a wavelength of 510 nm. The molar adsorption coefficient at this wavelength is 1150 $M^{-1}cm^{-1}$ (Bielski and Thomas 1987). These characteristics are helpful in the calculation of the concentration of ferrate solutions. Figure 2.3 shows the absorbance spectra of Fe (VI) in aqueous solution.

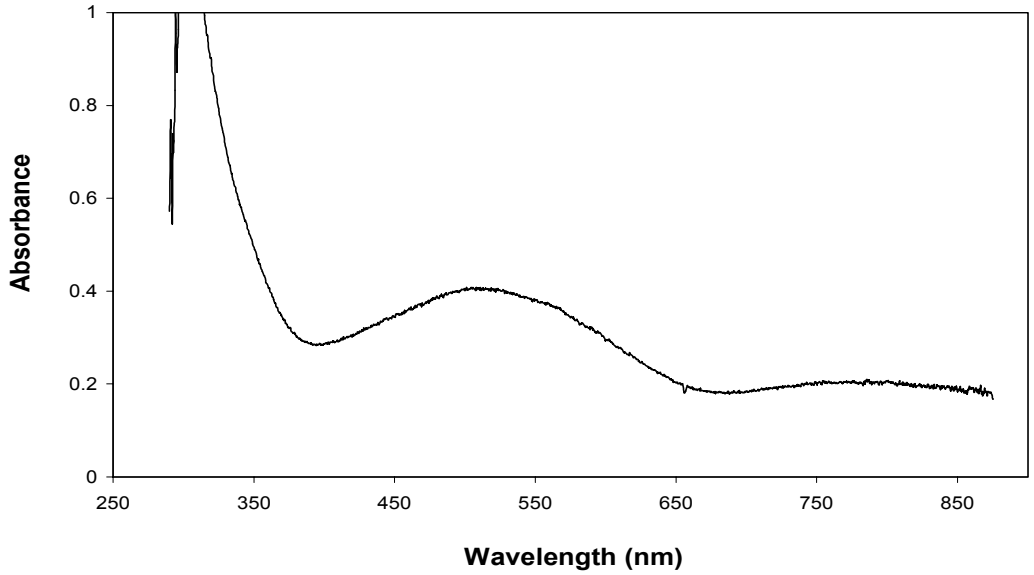


Figure 2.3 Absorbance Spectra of a 23.8 mg/L Solution of Fe(VI) Solution in Aqueous Solution at pH -9.2 (Adapted from: Lee et al., 2003).

The species distribution of Fe (VI) in aqueous solution is dependent on pH. Recent studies have demonstrated that there exist four Fe (VI) species in aqueous solution via their acid base equilibrium (Rush et al. 1989), $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-}. Figure 2.4 shows these four species and indicates that $HFeO_4^-$, and $FeO_4^2$are the predominant species in neutral and basic pH conditions respectively; where Fe (VI) is more stable.

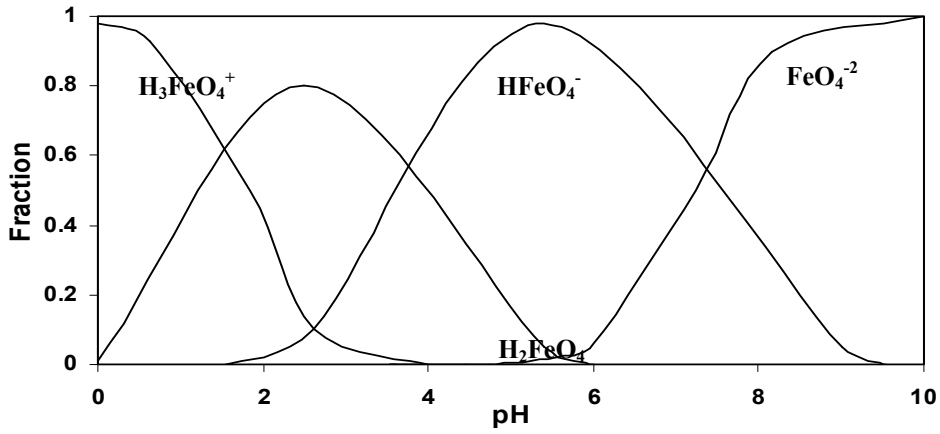


Figure 2.4 Species Distribution of Fe (VI) in Aqueous Solution (Adapted from: Lee et al. 2003).

2.4.3 Methods of Preparation

Three common methods of synthesis for the preparation of ferrate have been developed; wet oxidation, dry oxidation, and electrolysis. Using these methods ferrate has been prepared in the form of different salts such as Na_2FeO_4, K_2FeO_4, Ba_2FeO_4, Ag_2FeO_4. Of all these forms of ferrate, K_2FeO_4 has been most widely used and studied due to its relative easy preparation and its high stability (Lee et al.2003; Sharma 2002). The three principal methods of preparation are described below.

2.4.3.1 Wet Oxidation

This method consists of the oxidation of ferric ion by hypochlorite ion in a strong basic solution. This method has been used by several researchers for the preparation of K_2FeO_4 using chlorine gas and liquid sodium hypochlorite as sources of the hypochlorite

ion, and sodium hydroxide to maintain a basic solution (Thompson et al. 1951; White and Franklin 1998).

In general, the oxidation of ferric hydroxide by sodium hypochlorite in sodium hydroxide produces the liquid form of ferrate Na_2FeO_4, which is the form used in this research. The formation of solid K_2FeO_4 occurs when potassium hydroxide is added to the liquid ferrate and the K_2FeO_4 is precipitated. Equations 2.10 and 2.11 show the reactions.

$$2Fe(OH)_3 + 3\ NaOCl + 4NaOH \longrightarrow 2Na_2FeO_4 + 3NaCl + H_2O \qquad (2.10)$$

$$2Na_2FeO_4 + 4KOH \longrightarrow K_2FeO_4 + 2NaOH \qquad (2.11)$$

High purity potassium ferrate can be obtained using this method, within 96.9% reported by (Thompson et al. 1950). Researchers also reported that high purity reagents were required for the preparation of a pure solution of the ferrate given that the generated ferrate easily decomposes to ferric oxide in the presence of even small amounts of impurities such as transition metals (Schreyer and Ockerman 1952).

2.4.3.2 Dry Oxidation

This method consists of the treatment of iron oxides with oxidants such as Na_2O_2 at high temperature and pressure, as shown in Equation 2.12.

$$Fe_2O_3 + 3Na_2O_2 \longrightarrow 2Na_2Fe\,O_4 + Na_2O \quad (2.12)$$

This method has gained much attention recently as a green technology for the purpose of recycling various iron oxide wastes from steel manufacturing processes (Lee et al. 2003).

2.4.3.3 Electrolysis

Using electrolysis, ferrate can be prepared by anodizing a pure iron metal electrode in a concentrated alkaline solution. In this case, the purity of the generated ferrate depends on the current density, composition of anode material and types of electrolyte (Lee et al. 2003) The chemical reactions for this methods are illustrated on Equations 2.10 and 2.11.

$$\text{Anode: } Fe + 8OH \longrightarrow FeO_4^{-2} + 4H_2O + 6e^- \quad (2.10)$$

$$\text{Cathode: } 2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad (2.11)$$

2.4.4 Applications of Ferrate

In recent years considerable attention has been paid to various applications of Iron (VI) due to its novel properties as a powerful oxidant and the reduction of ferrate to a relatively non-toxic by-product, iron (III) (Sharma 2002). Researchers have documented its applications in environmental remediation processes as a green oxidant, coagulant,

disinfectant, and antifoulant (Gilbert et al. 1976; Lee et al. 2003; Sharma 2002). However, the main focus of research has been related to the treatment of drinking water and wastewater.

White and Franklin (1998) conducted a study using sodium ferrate as a reagent in drinking water treatment for the removal of color and manganese, and compared the results with ferric salts commonly used for such treatment. They concluded that ferrate had promise as a flocculant and that lower doses, in the range of 0.5 to 1 ppm, compared to 3 to 4 ppm required when ferric salts were used, could meet standards. They also evaluated the effect of pH on the effectiveness of ferrate and observed best color removal for secondary effluent at high pH conditions (above 8) and poor color removals at pH as low as 5.0. Therefore, these studies indicated that ferrate seemed to be more effective for water with a high pH.

Some other researchers reported that ferrate can be used during wastewater treatment for the removal of metals, non-metals, radionuclides, and reduction in turbidity (Waite 1978; De Luca and Cantelli 1992), and much attention has been paid in its applications for preoxidation to enhance coagulation. Ma and Liu (2002) reported that doses of ferrate ranging from 0.5 to 1.0 mg/l could remove turbidity and algae, and that ferrate preoxidation significantly enhanced the coagulation of waters, especially when the waters had a high organic content.

Another application of ferrate is its use as a disinfectant to purify water and wastewater. Investigations have shown that ferrate acts as a disinfectant for different type of microorganisms present in water such as fecal coliforms, Eschericha coli,

Sphaerotilus, Streptococcus, Salmonella, and Pseudomonas (Gilbert et al. 1976; Kazama 1995; Basu et al. 1987). It has been established that ferrate enters into the cells of the microorganisms causing inhibition of endogenous respiration (Kazama 1995).

Studies for the effectiveness of ferrate on virus destruction and removal have been conducted (Schink and Waite 1980; Kazama 1995). These studies have shown that ferrate rapidly inactivates virus *f2* at low concentrations and pH between 6 and 8 in water and secondary effluents. In addition, ferrate was proven as a useful biocide chemical to control biofouling (Waite and Fagan 1980).

Ferrate has also been used in the development of a *Super-iron Battery* in which ferrate replaces the commonly used manganese dioxide in the form of potassium ferrate. The potassium ferrate can absorb more electrons than the manganese dioxide cathode, and therefore the *super-iron battery* has high intrinsic energy and contains 47% greater capacity than the standard manganese dioxide battery (Sharma 2002).

2.5 Summary and Conclusions

Dewatering is a major component of the sludge handling processes and represents almost a 30 to 50 % of the total operational cost of a wastewater treatment plant. The reduction in cost and optimization for these operations is an issue that is always relevant to the management of a wastewater treatment plant. Dewatering is usually accompanied by chemical or physical conditioning processes which facilitate water removal by enhancing properties such as coagulation and flocculation of the sludge. The efficiency of

water removal depends to a great extend on the effectiveness of these coagulant agents.

Although research in the use of ferrate as an oxidant and coagulant for water and wastewater treatment has been done and its effectiveness during disinfection and turbidity removal process has been established, its application as a potential coagulant during sludge handling process has not been evaluated. Therefore the main purpose of this research is to study the effectiveness of ferrate during dewatering processes as a conditioning agent for anaerobic and waste activate sludges, and to evaluate the possibility of achieving dewatering and disinfection simultaneously in a single dosing and mixing unit process.

3 METHODS AND MATERIALS

This research was dedicated to the evaluation of ferrate effectiveness for biosolids dewatering. The research was divided into two parts; the evaluation of the ferrate effectiveness using centrifugation and filtration, and the comparison of ferrate with ferric and polymer conditioners currently used at the wastewater treatment plants where the samples were collected. This chapter provides a description of the experimental and analytical techniques used for this research. The first part of the chapter is dedicated to the production of ferrate and the second part describes the experiments conducted for the evaluation of the ferrate effectiveness, and its comparison with ferric and polymer.

3.1 Preparation of Sodium Ferrate

The wet oxidation method was used for the preparation of the ferrate used during this research (Thompson et al. 1951; White and Franklin 1998). This section discusses the procedure followed for the preparation of the ferrate solution and the analytical techniques used to determine ferrate concentration.

3.1.1 Materials

3.1.1.1 Chemicals

The reagents used for the preparation of ferrate were industrial grade chemicals. A 13.9% by wt (as OCl^-) solution of sodium hypochlorite was obtained from Odyssey Manufacturing (Tampa, Fl).The solution was stored in the dark at 4°C to prevent decomposition from the effect of light and high temperatures. Solutions of 50% by wt sodium hydroxide and 40% by wt ferric chloride were obtained from Brentag Mid-South, Inc. (Tampa, Fl). The solutions were stored in 1-gallon polyethylene containers at room temperature (25°C).

For the preparation of the buffer solution used for ferrate analysis, sodium tetraborate decahydrate and di-sodium hydrogen phosphate anhydrous were obtained from Fisher Scientific. These chemicals were laboratory grade and at least 99% pure.

3.1.1.2 Equipment

A jacketed 100-ml beaker was used as a reactor. The inlet and outlet of the jacket were connected with a 3/8-in ID tubing to an Isotemp Refrigerated Circulator (Fisher Scientific) to provide temperature control. The tubing was secured using 16 stainless-steel hose clamps. A picture of the system is shown in Figure 3.1. The circulator comes with stainless-steel 1/4 NPT inlet and outlet fittings with a 3/8-in ID serrated adapter, a

digital controller, heating/cooling controller indicators, a four-button key pad to adjust the temperature, and a Proportional Integral Derivative (PID) microprocessor control, which anticipates approach to temperature set point and prevents overshooting. The pumping capacity for the Refrigerated Circulator is 15 lpm; the reservoir for the fluid (water) has a capacity of 6 liters and a temperature range of -20 to 200 °C with a temperature stability of ±0.01°C.

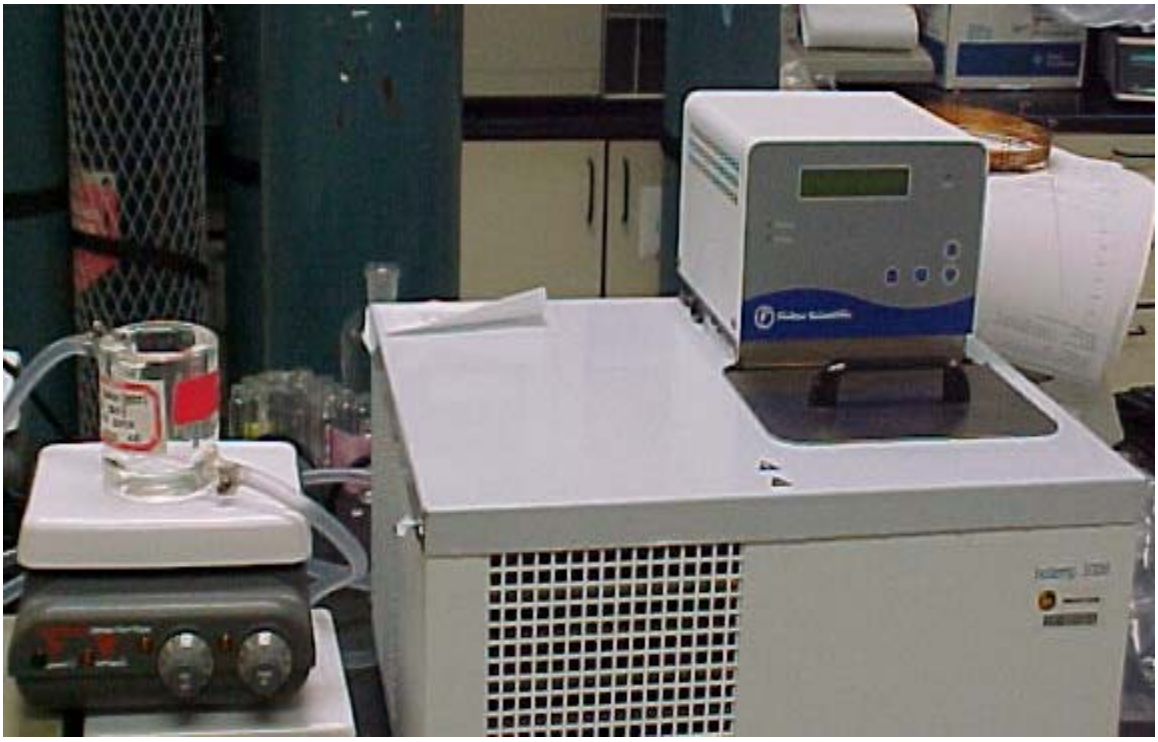


Figure 3.1 Experimental Setup for the Production of Ferrate.

A CHEM2000 UV-VIS spectrometer purchased from Ocean Optics (Dunedin, Fl) was used for the ferrate analysis. The wavelength range for the instrument is 200-850 nm. The spectrometer has a deuterium tungsten halogen light source and cuvette holder for 1-cm square cuvettes, and a light source/sample holder that connects to the spectrometer via optical fiber. A quartz cell was used for sample analysis. The specifications for the instrument and the cell are presented in Table 3.1 and Table 3.2, respectively.

Table 3.1 Specification for the Spectrometer

Parameter	Description/Value
Dimensions (mm)	Length: 190.0 Width: 104.9 Height: 40.9
Wavelength Range	200-850 nm
Optical resolution	~ 1 nm FWHM
Integration Time	3 milliseconds
Source Lamp	Deuterium
Path length	1 cm

Table 3.2 Specifications for the Quartz cell

Parameter	Description
Dimensions (mm)	Length: 12.5
	Width: 12.5
	Height: 45
Nominal volume	3.5 ml
Polished windows	2

3.1.2 Procedure

The method used for the preparation of sodium ferrate was the wet oxidation method (Thompson et al. 1951; White and Franklin 1998), which consists of the oxidation of ferric ion by hypochlorite ion in a strong basic solution. Two different procedures were used for the preparation using liquid (sodium hypochlorite) and solid (calcium hypochlorite) forms of hypochlorite.

A lab-scale reactor with capacity of 100 ml was used for the preparation of sodium ferrate. The reactor was connected to a temperature controller system that allows temperature adjustment as required, and a stir bar was used as a mixing device.

3.1.2.1 Sodium Hypochlorite

The desired temperature for the process was maintained using the temperature controller system. When the temperature was within 5°C of the desired temperature the

13.9% by wt sodium hypochlorite solution was poured into the reactor and mixed with a 50 % by wt solution of sodium hydroxide. A temperature increase of 3°C occurred due to the heat produced by the reaction between the sodium hypochlorite and the sodium hydroxide solution. Then, the ferric chloride was added slowly to the reactor while mixing.

3.1.2.2 Calcium hypochlorite

A solution with a concentration of 13.9% by wt as OCl^- was prepared by mixing calcium hypochlorite, sodium hydroxide, and distilled water. The desired temperature for the process was maintained using the temperature controller system. When the temperature was within 5°C of the desired temperature the 13.9% by wt hypochlorite solution was poured into the reactor. Then, the ferric chloride was added slowly to the reactor while mixing.

3.1.3 Analytical Technique

The concentration of the ferrate solution was quantified using a spectroscopic technique at the wavelength at which ferrate shows its maximum spectra (510 nm). The ferrate solution had to be diluted prior to analysis. Since the rate of decomposition of ferrate is affected by pH conditions, a buffer solution was used to dilute the sample. The solution was prepared by dissolving 0.3813 g of sodium tetraborate decahydrate and 0.7098 g of de-sodium hydrogen phosphate anhydrous in 1 liter of distilled water. This

solution buffers the ferrate sample at pH 8.0, where ferrate has high stability, thus ensuring reliable analytical results.

A sample of ferrate solution was taken from the reactor using a disposable pipette, and three drops of the solution were added to a beaker containing 50 ml of the buffer solution, without allowing it to strike the sides of the beaker. The 50-ml buffer solution is weighed prior to the addition of ferrate and after the addition of ferrate. The difference between the weights provides the weight of the sodium ferrate solution added. The ferrate-borax solution was then mixed and its absorbance was measured at 510 nm. The ferrate concentration of the solution is calculated using Beer's Law and the density of the solution using Equations 3.1 to 3.4.

$$A = \varepsilon l c \tag{3.1}$$

Where,

A = Absorbance (at 510 nm)

ε = Extinction coefficient (1150 $M^{-1}cm^{-1}$)

l = Cell path length (1 cm)

c = Concentration (M)

Thus, the concentration of the ferrate in the solution can be calculated from Equation 3.2.

$$c = \frac{A}{\varepsilon * l} \tag{3.2}$$

Knowing the ferrate concentration and the percent by weight of the ferric chloride solution initially used for the preparation of ferrate, the conversion yield in terms of iron can be calculated using Equation 3.3.

$$Yield = \frac{(P * S * 1000 * \varepsilon * \ell)}{(MW_{FeCl3} * V * A)} * 100\% \tag{3.3}$$

Where,

P = Percent of ferric chloride by weight (0.4)

S = Weight of ferrate sample (g)

MW_{FeCl_3}= 162.5 g/mole

V = Volume of buffer solution (50 ml)

The concentration of the ferrate solution is calculated using Equation 3.4.

$$[FeO_4^{-2}] = \frac{FeCl_3 * P * MW_{FeO_4}}{MW_{FeCl_3} * T} * yield * \rho \quad (3.4)$$

Where,

$[FeO_4^{-2}]$ = Ferrate Concentration (g/L)

$MW_{FeO_4^{-2}}$: = 119.85 g/mol

MW_{FeCl_3}: = 162.35 g/mol

Yield = Percentage conversion yield

ρ = Density of the ferrate solution (1.08 g/ml)

T = Total weight of the solution (g)

P = Percent of ferric chloride by weight (0.4)

$FeCl_3$ = Ferric Chloride solution (g)

3.2 Sludge Samples

Two different types of sludge were used for this study; anaerobic digested sludge and waste activated sludge, both collected from wastewater treatment plants located in Orange County, Fl. The samples of the anaerobic digested sludge were collected from the secondary anaerobic digester of the Southern Water Reclamation Facility, which has a capacity of 28 MGD and uses a five-stage Bardenpho nutrient removal system for its treatment. The sludge is treated by anaerobic digestion for stabilization at 35 °C and a residence time of 15 days. The samples of waste activated sludge were collected from

the secondary clarifier of the Eastern Water Reclamation Facility, which has a capacity of 11.4 MGD and uses a five-stage Bardenpho nutrient removal system.

Grab samples of the sludges were collected in 1-L polyethylene containers and all tests were started within two hours after sampling to prevent subsequent sludge changes. The total solids content, total suspended solids, and volatile solids were determined according to The Standard Methods for the Examination of Water and Wastewater (20^{th} Edition) Method No. 2540B, 2540D, and 2540 E, respectively. The pH and the temperature of the original sludge samples were measured as well, using an AR25 pH-meter and a mercury thermometer, both purchased from Fisher Scientific. Duplicate measurements were made and the average of the obtained values was reported as the final value for each parameter. The average values for each type of sludge are presented in Table 3.3.

Table 3.3 Properties of the Original Sludge Samples

Parameter	**Anaerobic Digested sludge (No of samples = 8)**	**Waste Activated Sludge (No of samples = 9)**
Total Solids	2.10 g/l	0.95 g/l
Total Suspended Solids	0.87 g/l	0.41g/l
Volatile Solids	0.20 g/l	0.31g/l
pH	7.20	6.72
Temperature	35°C	25°C

3.3 Conditioning of the Sludge

Samples of anaerobic digested sludge and waste activated sludge were conditioned using sodium ferrate prepared with sodium hypochlorite, sodium ferrate prepared with calcium hypochlorite, ferric chloride, ferric chloride with lime, polymer, and polymer and ferrate. For proper distinction of the two ferrate products used for this study, the ferrate prepared with sodium hypochlorite was called ferrate (Na^{+}) and the ferrate prepared used calcium hypochlorite was called ferrate (Ca^{+2}). The evaluation of biosolids dewatering after conditioning was conducted using centrifugation and the CST tests which are commonly used for preliminary evaluation of conditioning agents (Chu and Lee 2000;Guan et al. 2003; Gujar 2001; Shin et al. 1988).

3.3.1 Materials

Ferrate, ferric chloride, lime, and polymer solutions were used as coagulant agents to evaluate the effectiveness of ferrate alone, and its effectiveness compared to chemicals currently used during dewatering operations. The two ferrate solutions were prepared using the procedure described in Section 3.1. A 40% by wt ferric chloride solution with specific gravity of 1.432 obtained from Brentag Inc (Tampa, Fl), and 95% by wt slaked lime obtained from Fisher Scientific were also used for conditioning of the sludges.

Polymer solutions currently used at the wastewater treatment plants where the samples were collected were used for each type of the sludge. For the anaerobic digested sludge, a cationic water soluble C-6288 polymer obtained from Polydyne, Inc (Riceboro,

GA) was used, and a 2%v/v solution was prepared using distilled water as used at the Southern Water Reclamation Facility. For the waste activated sludge, a cationic Zetag 7848 polymer obtained from Fort Bend Services, Inc (Stafford, TX) was used, and a 0.3 %v/v solution was prepared to apply the polymer as used at the Eastern Water Reclamation Facility.

A 10-ml pipette and a 100-μL micro-pipette obtained from Fisher Scientific were used to add the coagulant agents to the samples of sludge. Hydrochloric acid and sodium hydroxide with concentrations of 38% by v/v and 50% by wt, respectively, were used for pH adjustment.

Ceramic-Top Stirring plates No S66327 purchased from Fisher Scientific with stirring speeds from 100 to 1000 rpm were used for sludge mixing. An Accumet Research/25 pH meter from Fisher Scientific was used to determine the pH.

3.3.2 Procedure

Sludge samples of 70 ml were placed in 100-ml beakers and stirred prior to conditioning for two minutes using a rotational speed of 100 rpm and 200 rpm for the waste activated sludge and the anaerobic digested sludge respectively, to assure homogeneous sludge samples. The rotational speed was increased to 750 rpm, and the coagulant agents were added under agitation using pipettes and micro-pipettes. The high mixing was maintained for one minute to assure complete contact between the coagulant and the sludge. Then, the rotational speed was decreased to 350 rpm and the mixing was

continued for two minutes to promote the agglomeration of the formed flocs. This procedure was used for the addition of all the coagulant agents (Langer et al. 1994). Six and eight different sets of experiments were conducted using the anaerobic digested sludge and the waste activated sludge, respectively. The volume of 70 ml for the sludge samples was selected based on the required volumes for the centrifugation and CST tests. For the CST test the required volume of conditioned sludge was 30 ml according to The Standard Methods for the Examination of Water and Wastewater (20^{th} Edition) Method No 2710G, which indicates that 6 ml of conditioned sludge and five readings per sample should be used. For the centrifugation test a volume of 40 ml was defined based on the capacity of the plastic cells available to place the sludge.

3.3.2.1 Anaerobic Digested Sludge

For the anaerobic digested sludge, seven different sets of experiments were conducted using different coagulant agents. In general, an individual set of experiments consisted on the addition of different doses or a specific dose of each type of coagulant for the conditioning of the sludge. A brief description of each set of experiments is presented below and summarized in Table 3.4.

- **Set I**: Doses of 0.5 to 7 g/l of the sodium ferrate product prepared using the procedure described in Section 3.1.2.1 were added to the sludge in order to define a range for the evaluation of the optimum dose.
- **Set II:**: Five different doses from 4 to 5g/l of the sodium ferrate product identified as

the range for the optimum dose in Set I were added to the sludge and pH of 7, 8, and no pH adjustment were used to define the optimum pH. The pH adjustment was done using 38% v/v hydrochloric acid

- **Set III:** Five different doses from 4 to 5 g/l of the ferrate (Na^{+}) product prepared using the procedure described in Section 3.1.2.1 were added to the sludge and the pH was adjusted to pH 7.0 (identified as optimum in Set II) after addition of ferrate using 38% v/v hydrochloric acid added to the conditioned sludge.
- **Set IV**: Doses of 50, 500, and 5000 mg/l of the ferrate (Ca^{+2}) product prepared using the procedure described in Section 3.1.2.2 was added to the sludge, and the pH was adjusted to pH 7.0 using 38% by wt hydrochloric acid.
- **Set V**: Doses of 23, 230, and 2300 mg/l as iron of ferric chloride which contained amounts of iron (Fe^{+3}) equal to those of iron (Fe^{+6}) present in the ferrate product used in Set IV were added to the sludge, and the pH was adjusted to pH 7.0 using 50% by wt sodium hydroxide.
- **Set VI**: Doses of 23, 230, and 2300 mg/l as iron of ferric chloride-lime solution containing the same amounts of iron and calcium present in the doses used in Set IV were added to the sludge. The pH was adjusted to pH 7.0 as well.
- **Set VII**: The polymer dose used for the Southern Water Reclamation was added to the sludge and no pH adjustment was used.

Table 3.4 Summary of Experiments for Anaerobic Digested Sludge

Set No	Coagulant	pH
I	Ferrate (Na^{+})	No pH adjustment
II	Ferrate (Na^{+})	pH: 7, 8 and 13.8
III	Ferrate (Na^{+})	pH adjustment (7.0)
IV	Ferrate (Ca^{+2})	pH adjustment (7.0)
V	Ferric chloride	pH adjustment (7.0)
VI	Ferric chloride-lime	pH adjustment (7.0)
VII	Polymer	No pH adjustment

3.3.2.2 Waste Activated Sludge

For the waste activated sludge, nine sets of experiments were conducted using different coagulant agents. In general, an individual set of experiments consists of the addition of different doses or a specific dose of each type of coagulant for the conditioning of the sludge. A brief description for each set of experiments is presented below and summarized in Table 3.5.

- **Set I**: Doses of 0.5 to 7g/l of the sodium ferrate product prepared using the procedure described in Section 3.1.2.1 were added to the sludge in order to define a range for the evaluation of the optimum dose.
- **Set II:**: Five different doses from 0.5 to 1.25g/l of the sodium ferrate product identified as optimum doses in Set I were added to the sludge and pH of 2.0, 3.0, 3.5, 5.0, 7.0, 8.0, and no pH adjustment were used to define the optimum pH. The

pH adjustment was done using 38% v/v hydrochloric acid

- **Set III:** Five doses ranging from 0.5 to 1.25 g/l of the sodium ferrate product prepared using the procedure described in Section 3.1.2.1 were added to the sludge and the pH was adjusted to pH 7.0 (identified as optimum in Set II) after addition of ferrate using 38% v/v hydrochloric acid added to the conditioned sludge.
- **Set IV**: Doses of 10, 100, and 1000 mg/l of the ferrate (Ca^{+2}) product prepared using the procedure described in Section 3.1.2.2 was added to the sludge, and the pH was adjusted to pH 7.0 using 38% by wt hydrochloric acid.
- **Set V**: Doses of 4.7, 47, and 470 mg/l as iron of ferric chloride containing amounts of iron (Fe^{+3}) equal to those of iron (Fe^{+6}) present in the ferrate product used in Set VI were added to the sludge, and the pH was adjusted to pH 7.0 using 50% by wt sodium hydroxide.
- **Set VI**: Doses of 4.7, 47, and 470 mg/l as iron from ferric chloride-lime solution containing the same amounts of iron and calcium present in the doses used in Set IV were added to the sludge. The pH was adjusted to pH 7.0 as well.
- **Set VII**: A combination of the different doses of the 0.3% by v/v polymer solution used in the Eastern Water Reclamation Facility and a fixed dose of 0.258 g/L of sodium ferrate prepared using the procedure described in Section 3.1.2.1.were added to the sludge. The polymer was added first followed by the ferrate solution.
- **Set VIII:** The same polymer-ferrate combination was used and the pH was adjusted to

pH 7.0 using 38% by v/v hydrochloric acid.

- **Set IX** The polymer dose used at the Eastern Water Reclamation Facility was added to the sludge, and no pH adjustment was provided.

Table 3.5 Summary of Experiments for Waste Activated Sludge

Set No	Coagulant	pH
I	Ferrate (Na^{+})	No pH adjustment
II	Ferrate (Na^{+})	pH: 2.0, 3.0, 3.5, 5.0, 7.0, 8.0, and no pH adjustment
III	Ferrate (Na^{+})	pH adjustment (7.0)
IV	Ferrate (Ca^{+2})	pH adjustment (7.0)
V	Ferric chloride	pH adjustment (7.0)
VI	Ferric chloride-lime	pH adjustment (7.0)
VII	Polymer-ferrate	No pH adjustment
VIII	Polymer-ferrate	pH adjustment (7.0)
IX	Polymer	No pH adjustment

After conditioning of the sludge microscopic pictures of the sludge flocs were obtained using a phase-contrast microscope at magnification of 1000Xin all set of experiments.

3.3.2.3 Doses

For the ferrate solution different concentrations in mg/l of ferrate as FeO_4^{-2} based on the preliminary experiments results presented in Appendix A were used to determine the optimum dose based on centrifugation and CST tests. The volume of ferrate solution needed for each specific dose was calculated using Equation 3.5.

$$V_{Ferrate} = \frac{C_1 * V_1}{C_2} \tag{3.5}$$

Where,

$V_{Ferrate}$ = Volume of ferrate solution (ml)

V_1 = Sludge sample (70 ml)

C_1 = Ferrate Dose Concentration as FeO_4^{-2} (mg/l)

C_2 = Ferrate solution concentration as FeO_4^{-2} (mg/l)

The doses of ferric chloride were established to maintain the same iron concentration as those used in ferrate treatment (Fe^{+6}). The required volumes were calculated using Equation 3.6 and Equation 3.7.

$$[Fe] = \frac{C_1 * MW_{Fe}}{MW_{FeO4}} \tag{3.6}$$

Where,

[Fe] = Concentration as iron in ferrate dose (mg/l)

C_1 = Ferrate dose concentration as FeO_4^{-2} (mg/l)

MW_{Fe} = 55.8 g/mol

$MW_{FeO_4^{-2}}$ = 119.85 g/mol

Then,

$$V_{Ferric} = \frac{[Fe] * V_1}{C_3} \tag{3.7}$$

Where,

V_{Ferric} = Volume of 40% ferric chloride solution (ml)

V_1 = Sludge sample (70 ml)

[Fe] = Iron in ferrate dose (mg/l)

C_3 = Ferric chloride dose concentration as iron (mg/l)

The amount of lime used for the experiments was calculated using Equation 3.8.

$$Lime = \frac{Ca_F}{P} \tag{3.8}$$

Where,

Lime = Mass of lime that has to be added to the sludge with the 40%by wt ferric chloride (g)

Ca_F = Amount of calcium present in the ferrate dose (g)

P = Purity of the lime (0.95)

The polymer dose for the anaerobic sludge was 28 mg/l of 2% by v/v polymer solution, which is the polymer dose used by the wastewater treatment plant in its dewatering process. For the waste activated sludge doses varying from 0.0082 to 0.05 mg/l (used for the wastewater treatment plant) of 0.3% by v/v polymer solution were used.

3.4 Centrifugation

3.4.1 Materials

An arm centrifuge model Centra- HN purchased from International Equipment Company (USA) was used to experimentally evaluate the centrifugal effectiveness of the separation of water from the sludge after conditioning with sodium ferrate, calcium ferrate, ferric chloride, ferric chloride-lime, polymer , and ferrate with polymer. A HACH DR/4000 UV spectrophotometer (Loveland, Colorado) with a 1-in glass cell was used to evaluate the clarity of the supernatant after centrifugation. The specifications for these instruments are presented on Table 3.6 and Table 3.7.

Table 3.6 Specifications for the Centra-HN Centrifuge

Parameter	Description
Capacity	24 x 15 ml
Maximum tube size	Diameter: 3.0 cm Length: 13.3 cm
Maximum speed	9000 rpm
Maximum force	3400xG
Speed control	Variable
Maximum holding time	50 minutes
Dimensions	Diameter: 41 cm Height: 36 cm

Table 3.7 Specifications for the DR/ 4000 UV Spectrophotometer

Parameter	Description
Wavelength range	190 to 1100 nm
Wavelength Resolution	0.1 nm
Source Lamp	Deuterium
Dimensions	Length: 29 cm Width: 42 cm Height: 16 cm

3.4.2 Analytical Technique

The centrifuge was operated at three different rotational speeds; 800, 1600, and 2400 rpm to identify the optimal rotational speed for each type of conditioned sludge.

Samples of 40-ml of conditioned sludge were placed into transparent plastic cells

for the centrifugation experiments. The volume occupied by the solids after centrifugation was recorded after 60, 300, 600, 1200, 1800, and 2400 seconds for all rotational speeds at different pHs to estimate the volume reduction for the sludge and the required time to achieve mechanical equilibrium. The time at which the volume occupied by the solids was no more than one percent of the preceding reading was considered as the time needed to achieve mechanical equilibrium. Subsequent tests were stopped at the time of equilibrium.

After centrifugation, the turbidity of the supernatant was measured by pouring 10 ml of the supernatant into the 1-in glass cell and using the HACH program No. 3750 for the spectrophotometer. This program uses a colorimetric technique, which measures the absorbance of the solution using a wavelength of 860 nm and expresses the turbidity of the sample as Formazin Attenuation Units (FAU).

3.5 CST Test

The Capillary Suction Time (CST) test was used to evaluate the sludge filterability. This test determines the rate at which water is being released from the sludge and provides a quantitative measure, reported in seconds, of how readily the sludge releases water.

The radial absorption of filtrate from a cylinder containing the sludge placed in the center of a sheet of chromatography paper is monitored. The paper extracts the water from the sludge sample by capillary action. The time required for the water to migrate

from 1.5 to 3.0 cm (two contact points) is defined as the capillary suction time. This time is recorded automatically by monitoring the electrical conductivity change between the two points which are in contact with the chromatography paper.

3.5.1 Materials

A CST unit model 294-01 and chromatography paper, Whatman No. 17 purchased from OFI Testing Equipment (Houston, TX) were used to conduct this test. The CST unit consists of three separate components; an acrylic filtration unit with three electrodes, a stainless steel cylinder (1-cm diameter in one end and 1.8 cm at the other) and a timer case. The acrylic unit has a circle in the center where the stainless steel cylinder can be inserted prior to adding the sludge sample. The timer case has an on/off switch, a button for resetting the circuits after a sample has been analyzed, a finish lamp, and a 6-digit LCD counter which indicates the time in tenths of a second. A picture and a schematic of the instrument are presented on Figure 3.2 and Figure 3.3.

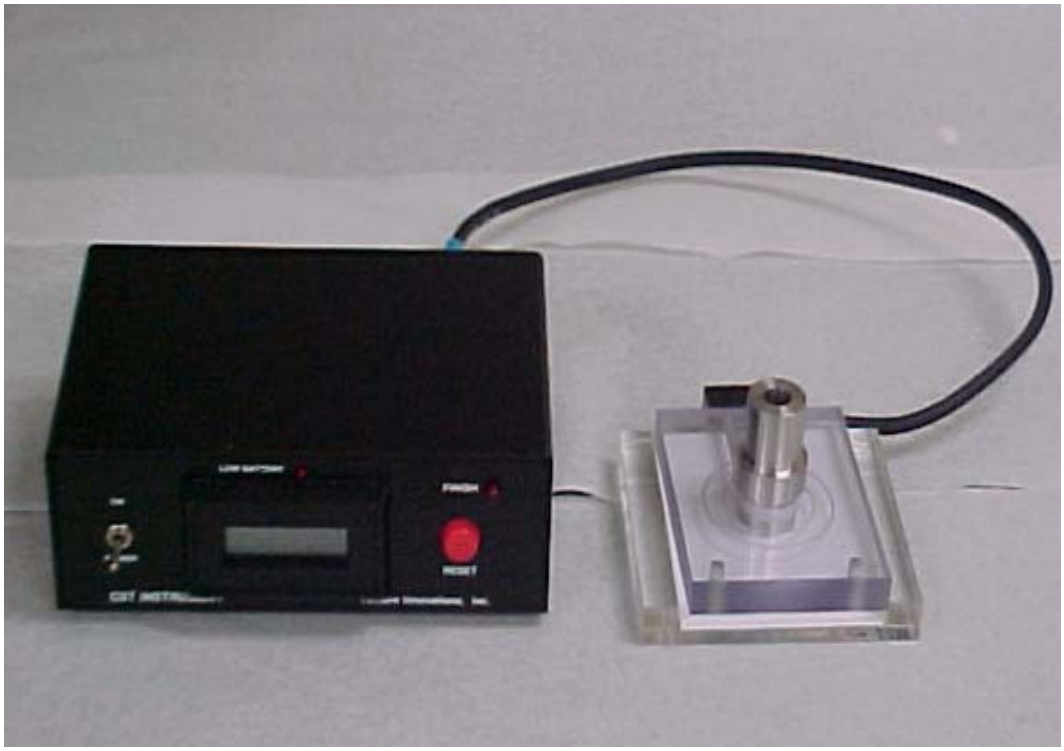
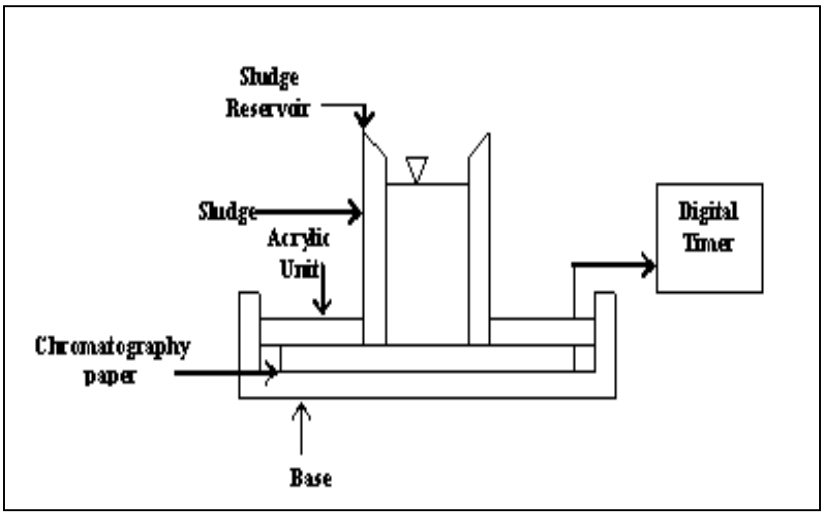
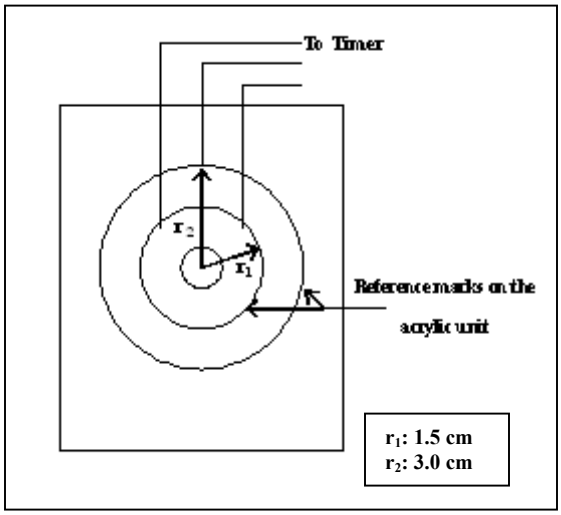


Figure 3.2 Capillary Suction Test Unit – Model 294-01

When the sample is placed in the cylinder; the liquid progresses in circular pattern. The timer starts when the liquid reaches the first pair of electrodes (radius 1.5 cm), and stops when the liquid reaches the third electrode (radius 3.0 cm). At this point the detector signals audibly indicating that the time on the screen corresponds to the CST time for the sample.



(Profile)



(Plan)

Figure 3.3 Schematic of the Capillary Suction Time Instrument. Adapted From: Standard Methods for the Examination of Water and Wastewater (20th Edition)

3.5.2 Analytical Technique

After resetting the CST meter. The stainless steel cylinder was placed on the center of the acrylic unit and 6.0 ml of the conditioned sludge were poured into the cylinder using a 10-ml pipette. The timer starts counting when the liquid reaches the first pair of electrodes. The time displayed on the 6-digit LCD when the signal is sounded is recorded as the CST time for the sample.

This procedure is repeated five times for each sample to account for measurement variation and identification of faulty reading due to leaks or spills. The average of those five readings is reported as the CST time for the sample.

4 RESULTS AND DISCUSSION

The objectives of this research were to evaluate the effectiveness of ferrate in the conditioning of biosolids. During this research, experiments were conducted to quantify the volume reduction of the sludge and the filtration time after conditioning using centrifugation and the Capillary Suction Time test, respectively. This chapter provides the results of these experiments, as well as additional experiments conducted to compare the effectiveness of ferrate with polymer and ferric chloride currently used in dewatering operations. A cost analysis for the conditioning of the sludge using ferrate is also presented.

4.1 Dewatering: Preliminary Experiments

Initial experiments were dedicated to determining the optimal rotational speed for centrifugation and pH based on the volume reduction of the sludge, the clarity (turbidity) of the supernatant, and the CST time for filtration. The ferrate doses used for these experiments were doses that provided highest reduction of volume for waste activated and anaerobic digested sludges during preliminary experiments. The results for these experiments are presented in Appendix A. The ferrate was prepared using the method described in Section 3.1.2.1.

4.1.1 Centrifugation

4.1.1.1 Rotational Speed Effect

To examine the effects of the rotational centrifugation speed on the dewatering of anaerobic digested and waste activated sludges conditioned with ferrate, a series of experiments were run using three different rotational speeds; 800, 1600, and 2400 r.p.m.. Five different doses of ferrate were used to condition the sludge and the volume occupied by solids over time was recorded at each rotational speed. The optimal rotational speed was defined as the rotational speed at which the volume reduction reaches a maximum value (Chu and Lee 2000).

For the waste activated sludge it was observed that the lowest volume occupied by solids was attained when the lowest rotational speed was used, as illustrated in Figure 4.1. The volume occupied by solids at 800 r.pm. was 2.5ml for a dose of 1g/l compared to 4.2 ml at 2400 r.p.m. These results indicated that an increase of a rotational speed from 800 to 1600 or 2400 r.p.m. will have a detrimental effect on dewatering of the conditioned sludge. It was also observed that an increase in the rotational speed impaired volume reduction not only for the conditioned sludge, but for the unconditioned sludge indicating that the rotational speed affects the physical properties of the sludge.

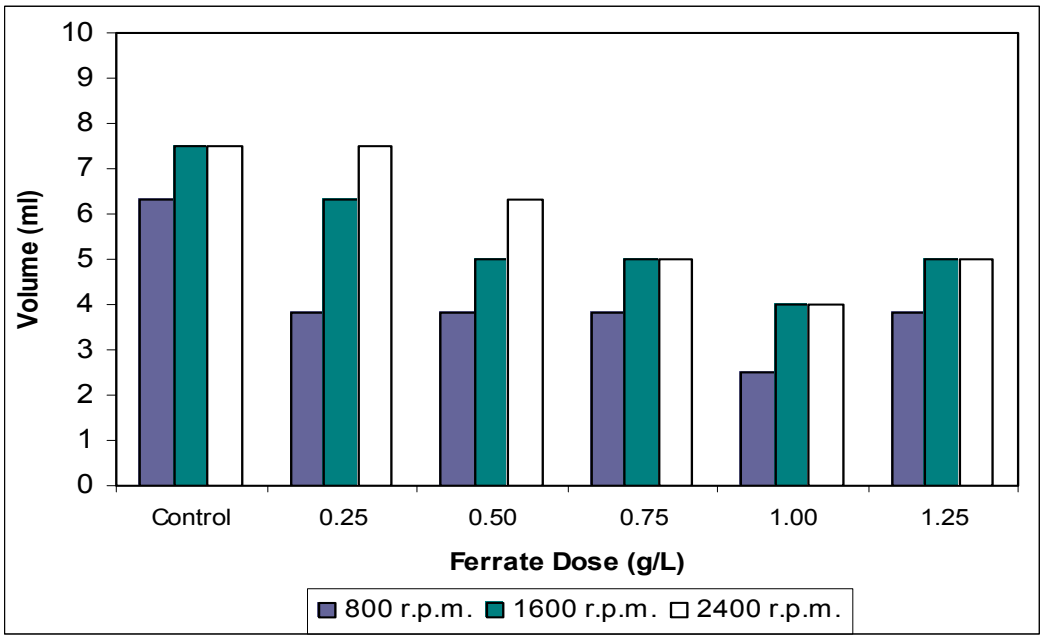


Figure 4.1 Volume Occupied by Solids at Different Rotational Speed Conditions for Waste Activated Sludge Conditioned with Ferrate.

Poor volume reduction when the rotational speed is increased is probably due to the extraction of the extracellular polymers from the sludge. These polymers provide the integrity and rigidity of the floc, holding all the components of the sludge matrix together. Researchers investigating the effect of centrifugation on physical properties of activated sludge have found that extraction of the extracellular polymers increases proportionally with an increase in rotational speed, and that the rigidity of the floc decreases as these polymeric substances are removed (Sanin and Vesilind 1994). Some other researchers who investigated the centrifugal separation of water from activated sludge subject to cationic polyelectrolyte flocculation found that water extraction was

significant at 400 to 700 r.p.m and limited or reduced at 1000 r.p.m. (Chu and Lee 2000).

For the anaerobic digested sludge the lowest volume occupied by solids was attained when the maximum rotational speed was used for all the doses, as shown in Figure 4.2. These results show that an increase in rotational speed improves the water removal from the sludge and reduces the volume occupied by solids by 45% when the rotational speed is increased from 800 rpm to 2400 rpm. These results were opposite to those obtained for the waste activated sludge. Release of the exocellular polymers has already occurred during anaerobic digestion (Novak et al. 2003). Thus, an increase in rotational speed does not impact the solution biopolymers or deteriorate the volume reduction of the sludge. Instead, the solids settling velocity for the solids increases by increasing the rotational speed and greater volume reduction is obtained for the highest rotational speed.

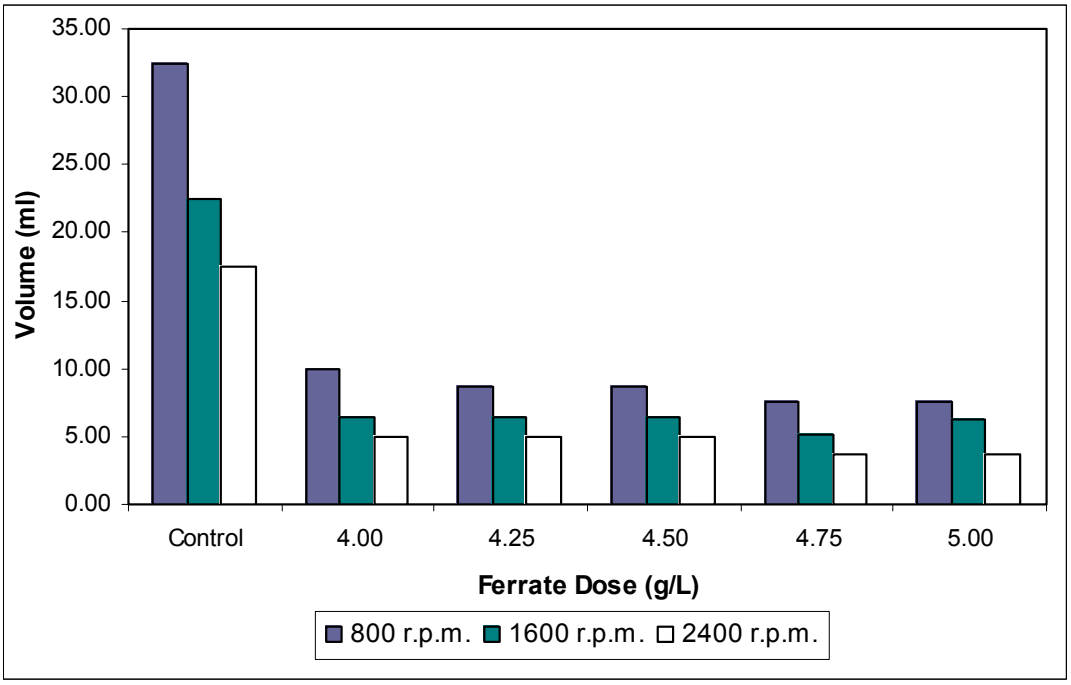


Figure 4.2 Volume Occupied by Solids at Different Rotational Speed Conditions for Anaerobic Digested Sludge Conditioned with Sodium Ferrate

Based on these results, 800 and 2400 r.p.m. were selected as optimal rotational speeds for evaluation of waste activated sludge and anaerobic digested sludge dewatering, respectively.

4.1.1.2 pH Effect

The experiments dedicated to investigate the pH effect on dewatering of the anaerobic and waste activated sludges were conducted using five different samples of conditioned sludge for each type of sludge.

For the waste activated sludge pH of 2.0, 3.0, 3.5, 5.0, 7.0, and 8.0, as well as the unadjusted pH after ferrate addition were evaluated. The volume occupied by solids was recorded over time, and the turbidity of the supernatant was recorded after centrifugation. A pH of 7 and 8 was used for the anaerobic digested sludge.

As shown in Table 4.1, the lowest volume occupied by solids for the waste activated sludge was attained for pH above 5 and dosages about 1g/l. Ferrate is reduced to ferric ion when it is added to the sludge. When ferric iron is present, the hydroxoiron (III) complexes and solid species of $Fe(OH)_3$ are formed at pH above5. These species are reported to be highly effective conditioning agents and may be responsible for the observed results (Shin et al. 1988).

Table 4.1 Volume Occupied by Solids at Different pH conditions for Waste Activated Sludge Conditioned with Ferrate.

pH	Dose (g/l)					
	0.00 (ml)	**0.25 (ml)**	**0.5 (ml)**	**0.75 (ml)**	**1.0 (ml)**	**1.25 (ml)**
2.0	11.0	8.75	7.50	7.50	7.50	7.50
3.5	11.0	8.75	7.50	7.50	6.50	7.0
5.0	11.5	7.50	7.50	7.50	6.00	6.30
7.0	12.5	7.50	7.50	7.50	5.00	5.00
8.0	12.5	7.50	7.50	6.25	5.00	4.90
13.6 (No adjustment)	12.5	7.50	7.30	5.50	5.00	5.00

The clarity of the supernatant was evaluated as well by measuring its turbidity after centrifugation. The data presented in Figure 4.3 indicate that lowest turbidity was attained at pH 2.0 and the highest turbidity was attained when pH was not adjusted (pH=13.6). This phenomenon may occur because the solubility of the ferric species increases as the pH decreases. Also, at pH greater than 9.5 hydrolysis of sludge solids increases and particles become suspended in the supernatant (Shin et al. 1988;Tixier et al., 2003).

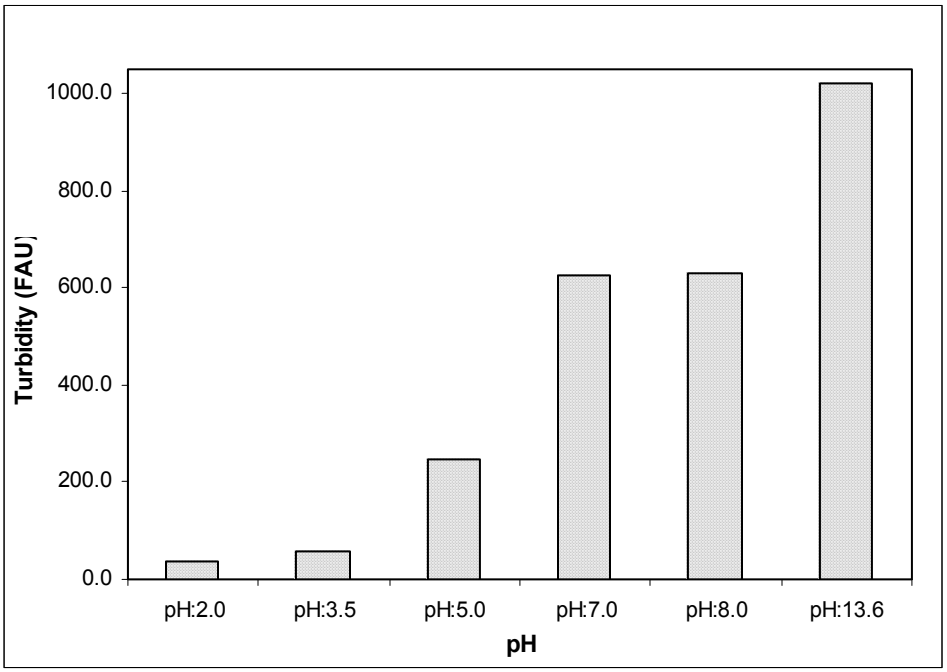


Figure 4.3 Turbidity at Different pH for Waste Activated Sludge Conditioned with Sodium Ferrate.

Although the lowest turbidity was observed at pH 2.0, this is not a feasible value for sludge treatment, particularly when considering land application because acidity would be introduce into the soil. This acidity reduces crops and pasture yields (McFarland 2000). Furthermore, the EPA Part 503 Rule for land application for biosolids requires pH of 5.5 to 7.5 to minimize metal leaching and maximize crop growing conditions (USEPA 1993). Therefore, the optimum pH selected was 7.0, which is within the regulated pH range and offers reasonable reduction in the volume occupied by solids.

For anaerobic digested sludge, pH above 7.0 was used for each of the four doses of ferrate used to condition the sludge. During the adjustment of pH foaming occurred at pH below 7.0, and sludge spilled. Therefore, a pH below 7.0 was not evaluated for this type of sludge. Figure 4.4 shows that, pH above 7.0 does not impact the volume occupied by the solids when ferrate is used for conditioning. Therefore, any of these pH conditions could be used for conditioning with ferrate.

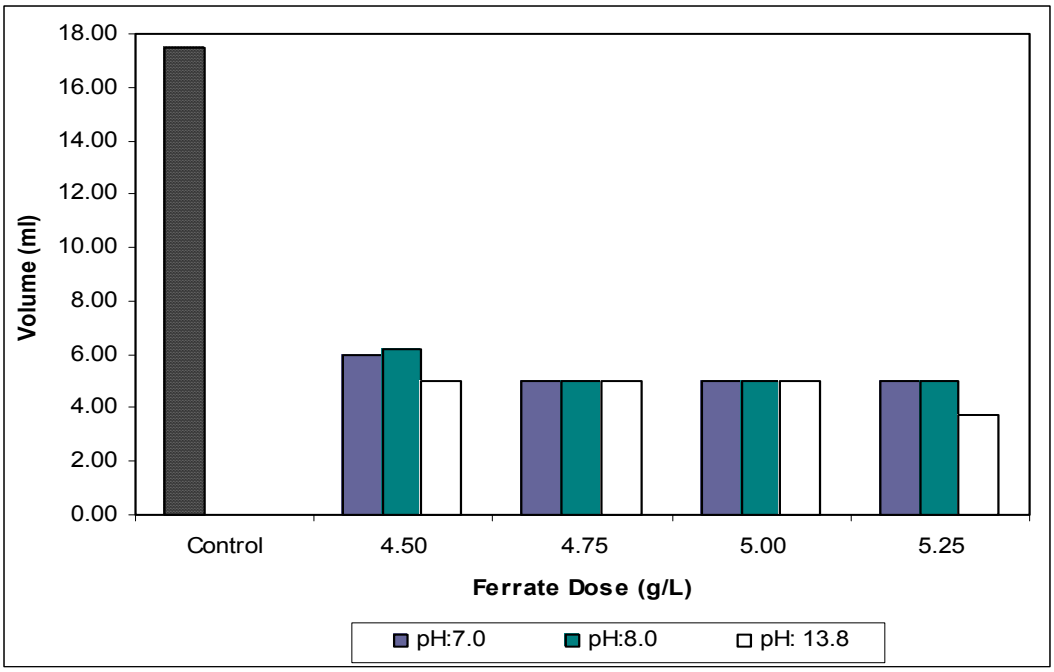


Figure 4.4 Volume Occupied by Solids for Anaerobic Digested Sludge Conditioned with Ferrate at Different pH conditions.

The turbidity data shown in Figure 4.5 indicate that the lowest turbidity was observed for pH 7. Since this pH offers the lowest turbidity and falls within the pH range required for land application of biosolids, it was selected as the optimum pH for dewatering of anaerobic digested sludge.

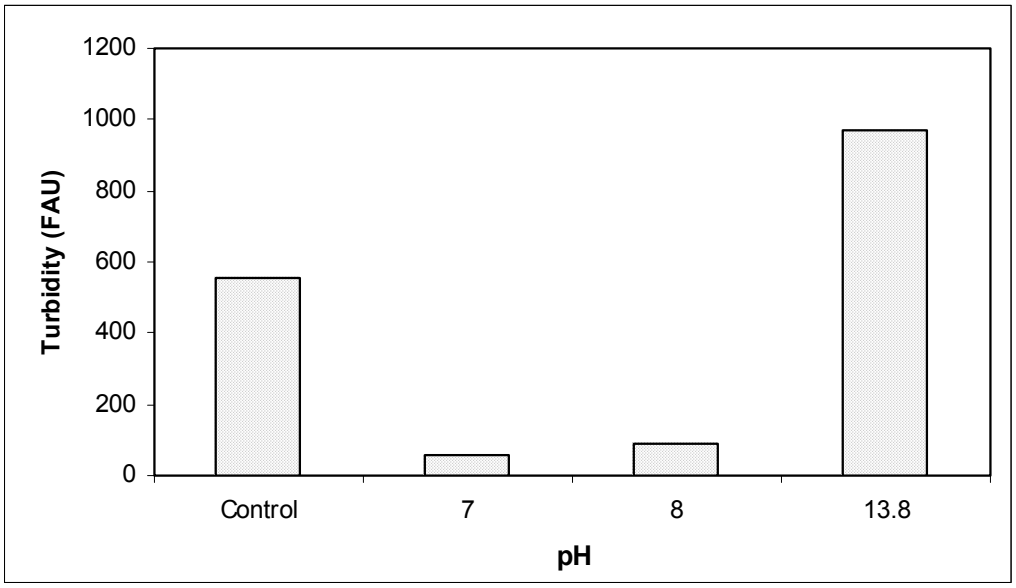


Figure 4.5 Turbidity at Different pH Conditions for Anaerobic Digested Sludge Conditioned with Ferrate.

4.1.1.3 Time Effect

After rotational speed and pH conditions were established, the time required to achieve mechanical equilibrium, as defined in Section 3.4.2, was determined by recording the percent volume occupied by solids at different times for each type of sludge. Times of 300, 600, 1200, 1800 and 2400 seconds were used.

As is displayed in Figure 4.6, the mechanical equilibrium for the waste activated sludge was achieved at 1200 sec when ferrate doses of 0.5, 0.75, and 1.25 g/l were used, and at 1800 sec when doses of 0.25 and 1.0 g/l were used. These results indicate that this time can vary from dose to dose and that the mechanical equilibrium would be achieved between 1200 and 1800 sec. Based on these results it was decided that the maximum

time required to record the volume occupied by solids when selecting the optimum dose should be 1800 sec.

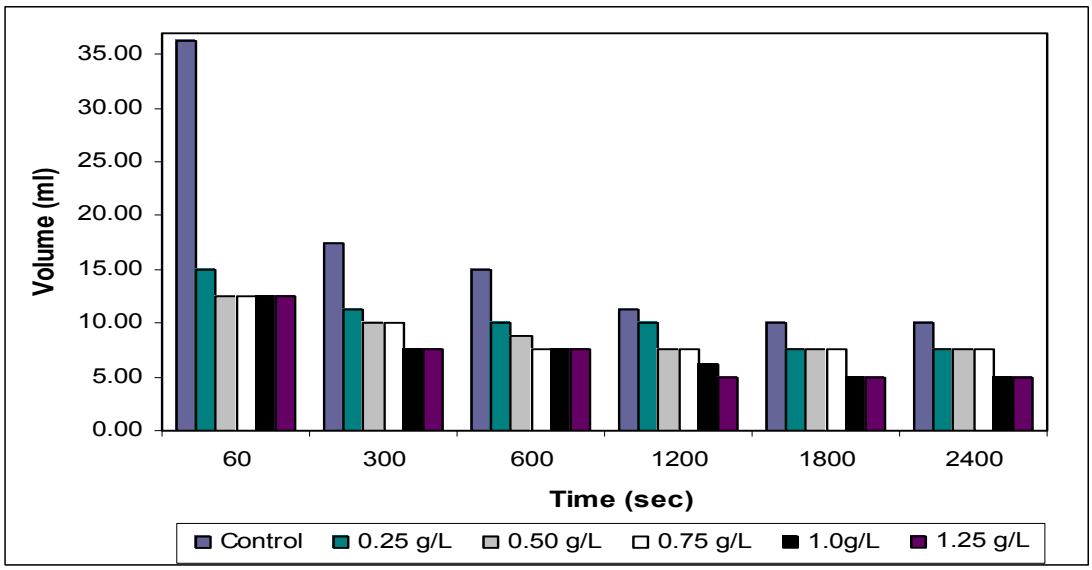


Figure 4.6 Volume Occupied by Solids at Different Times for Waste Activated Sludge Conditioned with Ferrate at pH 7.0 and 800 r.p.m.

For the anaerobic digested sludge, the mechanical equilibrium was achieved at 1800 sec when ferrate doses of 4.75, 5.0 and 5.25 g/l were used and at 1200 sec when 4.5 g/l were used, as illustrated in Figure 4.7. Since the mechanical equilibrium for most of the doses was attained at 1800 sec, this time was selected as the required time to achieve mechanical equilibrium and desired to evaluate the volume occupied by solids when selecting the optimum dose.

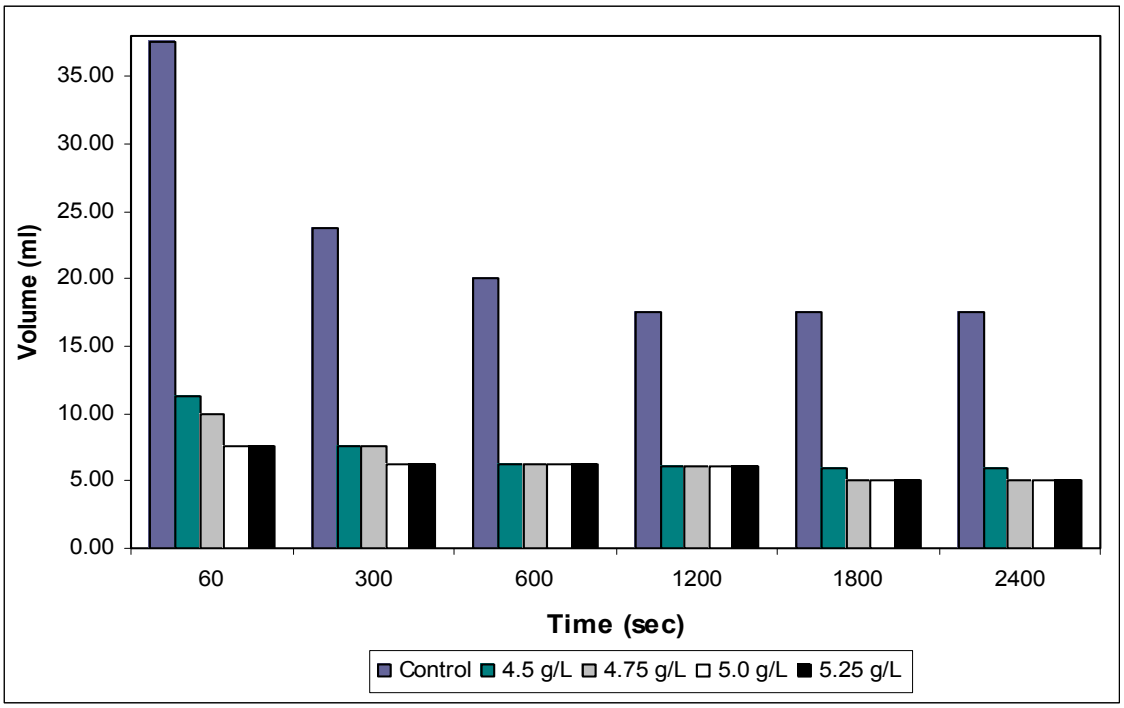


Figure 4.7 Volume Occupied by Solids at Different Times for Anaerobic Digested Sludge Conditioned with Ferrate at pH 7.0 and 800 r.p.m.

4.1.2 CST Experiments

The filterability of the sludge after conditioning was evaluated using the CST test described in Section 3.5, and the same ferrate doses used for centrifugation. Initially the filterability of the sludge was evaluated without pH adjustment and CST times ranging from 2450 to 3500 sec were obtained for the conditioned waste activated sludge, while the CST for the control was 20.5 sec. For the anaerobic sludge values ranging from 4350 to 5215 sec were observed, while the CST for the unconditioned sludge was 347.6 sec. Based on the turbidity results obtained during the centrifugation experiments when no pH

adjustment was used (pH=13.8), and knowing that the solubility of the formed ferric hydroxide species after the addition of ferrate decreases as the pH increases, it was concluded that the filter used for the test must be clogging due to the presence of these species. Therefore, pH adjustment was required in order to increase the solubility of those chemical species and improve the filterability of the conditioned sludge. Subsequent experiments were conducted using the same ferrate doses and the same pH as those used for the centrifugation test.

The results presented in Figure 4.8 show that for the waste activated sludge the CST decreases as the pH decreases, which indicated that the solubility of the resulting ferric species was interfering with the filterability of the conditioned sludge. However, it was also observed that for the same pH condition as the dose increased the filterability decreased, even though the pH was optimum for the solubility of ferric species. These results were opposite to the centrifugation results. For centrifugation, as the dose was increased the effectiveness of ferrate for centrifugation increased. This comparison indicates that the filter was clogged during filtration not only because of the insoluble ferric particles at high pH, but because another particulate source may have interfered with filtration. Since ferrate is considered a strong oxidant which reacts with organic substances (Gilbert et al. 1976; Lee et al. 2003; Sharma 2002), a possible explanation for this phenomenon is that ferrate may react with organics present in the sludge matrix resulting in breakdown of large molecules into smaller molecules, including biopolymers. Therefore, more turbidity is present when higher doses are used and the filter could clog. These results also indicated that contrary to centrifugation, for the waste activated sludge,

the effectiveness of filtration when ferrate is used depends not only on pH, but on ferrate concentration, and that less ferrate may be needed for conditioning when filtration is used for dewatering.

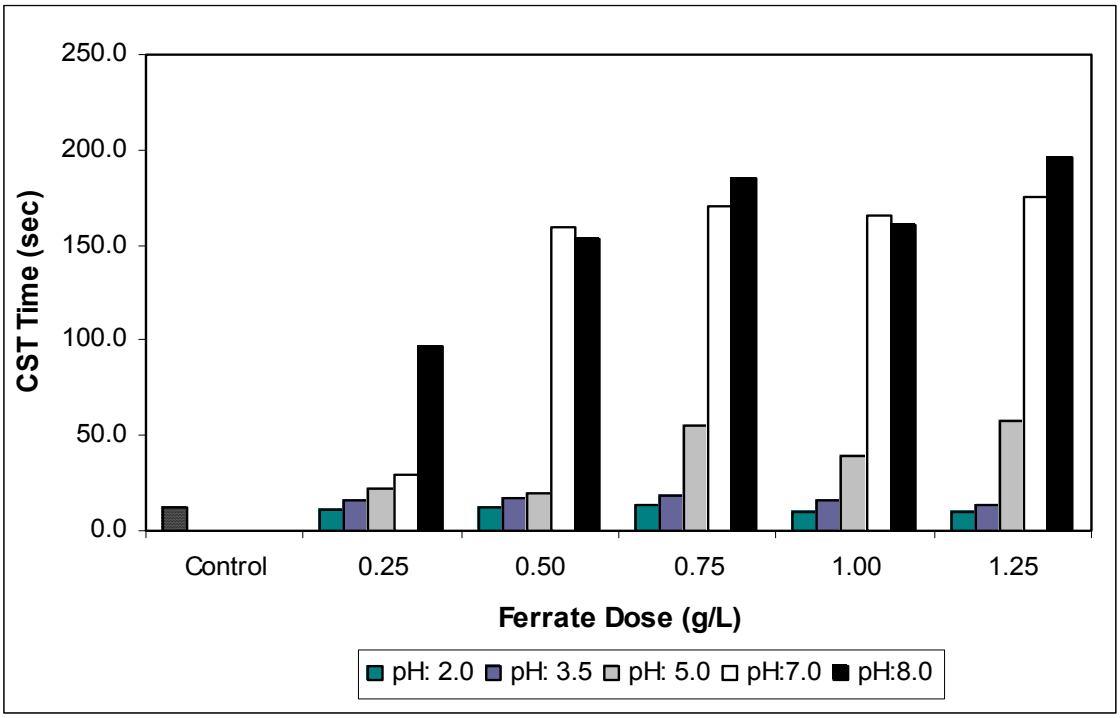


Figure 4.8 CST Times at Different pH conditions for Waste Activated Sludge Conditioned with Ferrate.

As shown in Figure 4.9, for the anaerobic digested sludge at pH 7.0 as the dose increases the filtration time decreases. However, at pH 8.0 the opposite effect is observed. A possible explanation for the difference may be that at pH 8.0 the ferric

hydroxide species are less soluble than at pH 7.0. Thus, when the dose is increased the filtration is reduced due to interference of these particles. It was also observed that for both centrifugation and filtration as the dose was increased the efficiency also increased at pH 7.0.

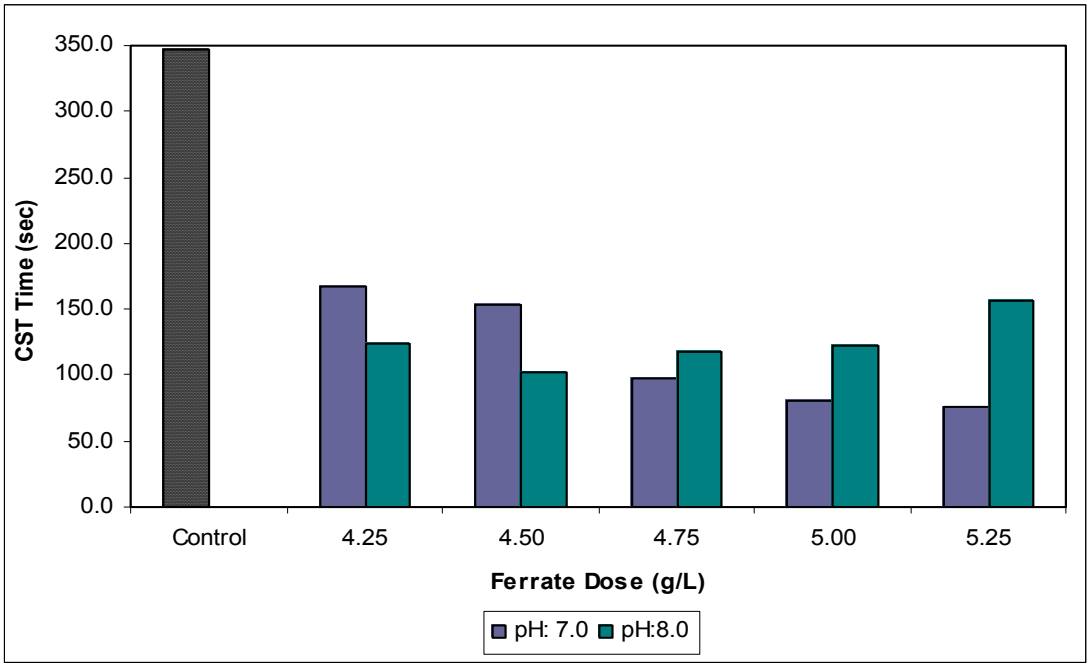


Figure 4.9 CST Times at Different pH Conditions for Anaerobic Digested Sludge Conditioned with Sodium Ferrate.

4.2 Optimum Doses

This section summarizes the optimum dose results for the centrifugation and filtration tests conducted using the optimum conditions of pH, time, and rotational speed. These results include the optimum ferrate dose for each type of sludge, a comparison of volume reduction and filtration time for several ferrate products, a comparison of properties for each type of sludge using ferrate and ferric, and a comparison of volume reduction and filtration time for ferrate with and without polymer.

4.2.1 Waste Activated Sludge

4.2.1.1 Optimum Dose

Centrifugation and filtration experiments were conducted using a rotational speed of 800 rpm and pH 7.0, which were defined as the optimum conditions during the preliminary experiments and ferrate doses varying from 2 mg/L to 1000 mg/L. These experiments were initially conducted using the ferrate product prepared with sodium hypochlorite and then were compared with results obtained for the ferrate produced using calcium hypochlorite.

As Figure 4.10 and Figure 4.11 reveal, the dose which provides the lowest volume occupied by solids during centrifugation was 1000 mg/l, which provides a 48% reduction in the volume occupied by the solids compared to a 12.5 ml for the control, and a 5.2%

solids in the cake compared to a 2.7% solids for the control. However, it was also observed that a dose of 10 mg/l provided a volume reduction of 40% compared to 12.5 ml for the control, and 4.5 % solids on the cake compare to 2.7% for the control. These results indicated that only a 0.7% increase on the solids on the cake would be obtained if a dose of 1000 mg/l is used instead of 10 mg/l. However, an increase of ferrate from 10 mg/l to 1000 mg/l would increase the cost 100 times. Therefore, 10 mg/l was selected as the optimum dose for centrifugation. Furthermore, when this dose provides the lowest turbidity as illustrated in Figure 4.12.

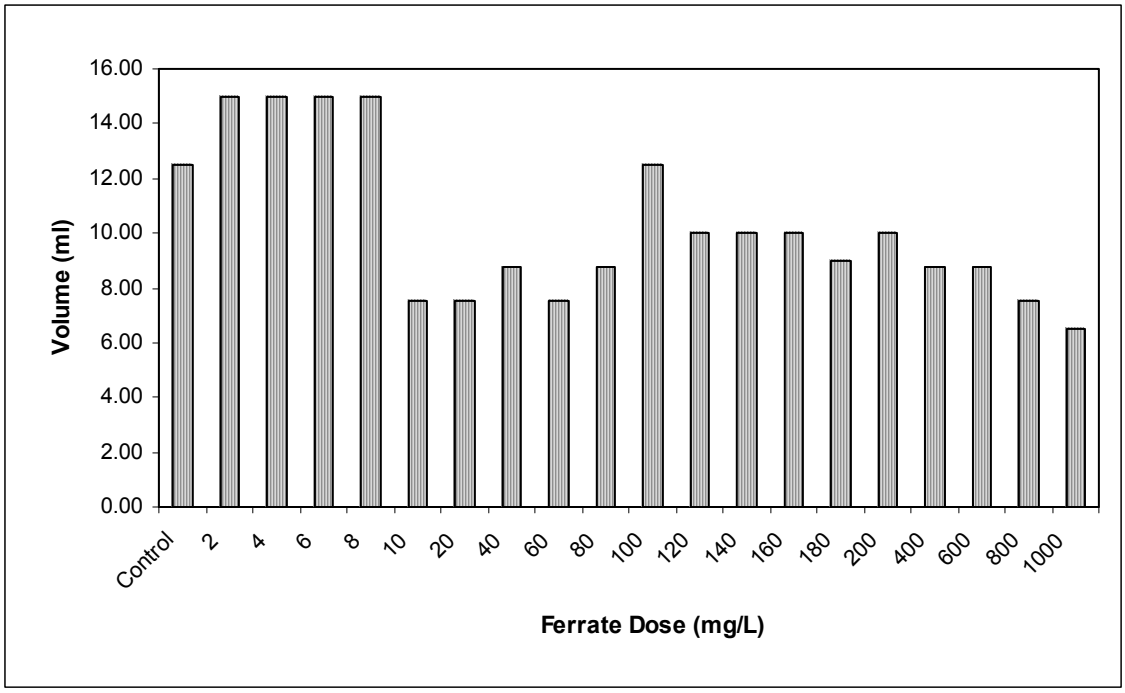


Figure 4.10 Volume Occupied by Solids for Waste Activated Sludge Conditioned with Sodium Ferrate.

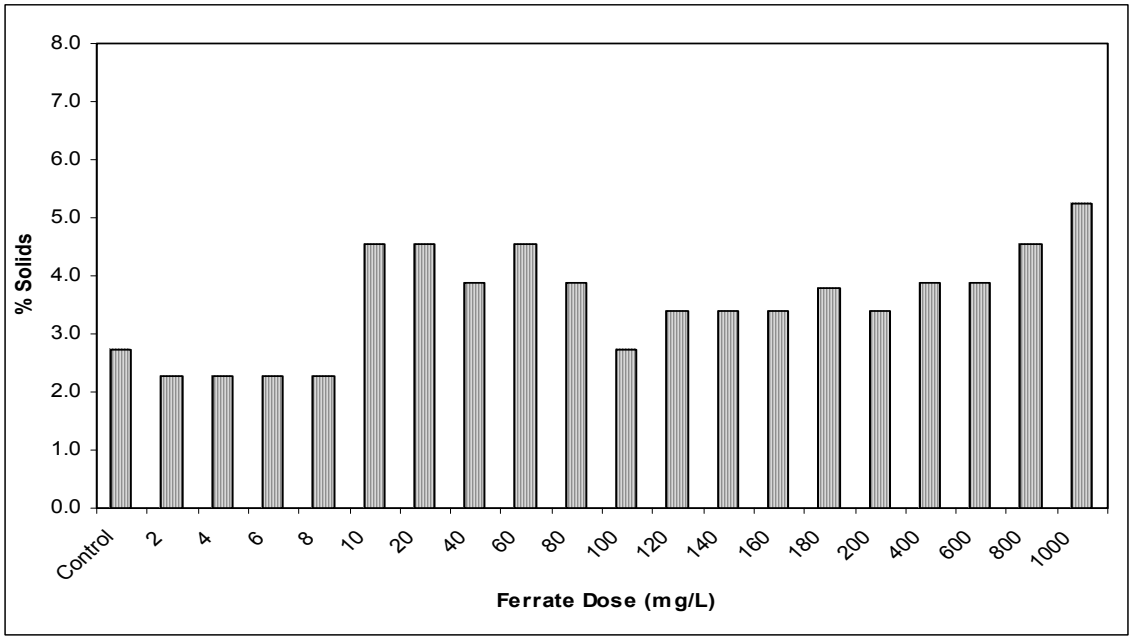


Figure 4.11 Percent of Solids in the Cake for Waste Activated Sludge Conditioned with Sodium Ferrate

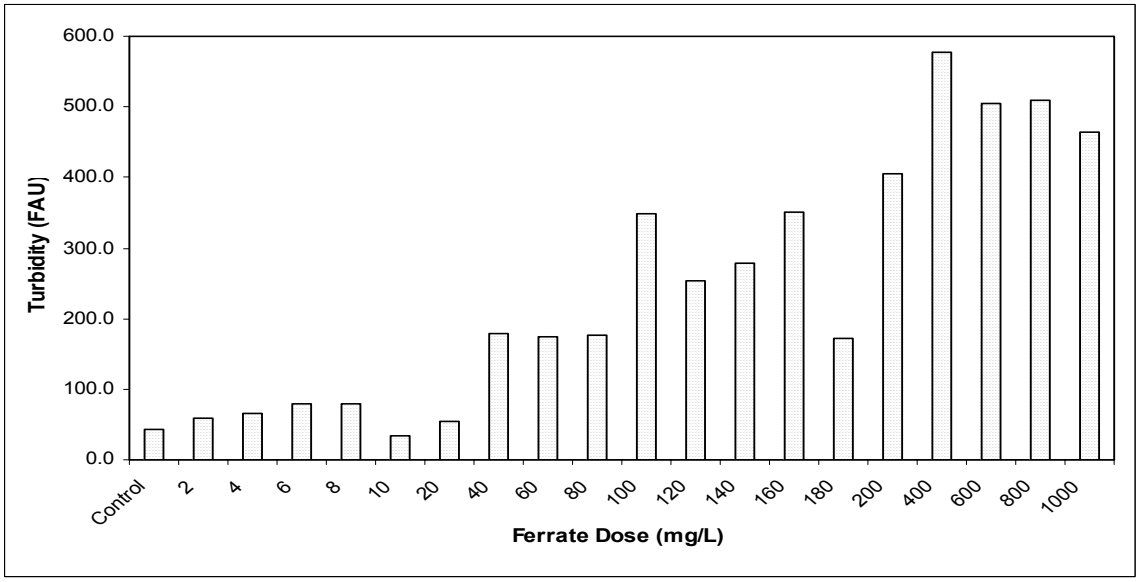


Figure 4.12 Turbidity of the Supernatant after Centrifugation for Waste Activated Sludge Conditioned with Sodium Ferrate

The CST results show that the optimum dose for filtration was 10 mg/L, which provides a 13.2 sec time of filtration compared to 22.6 sec obtained for the control. The results are presented in Figure 4.13.

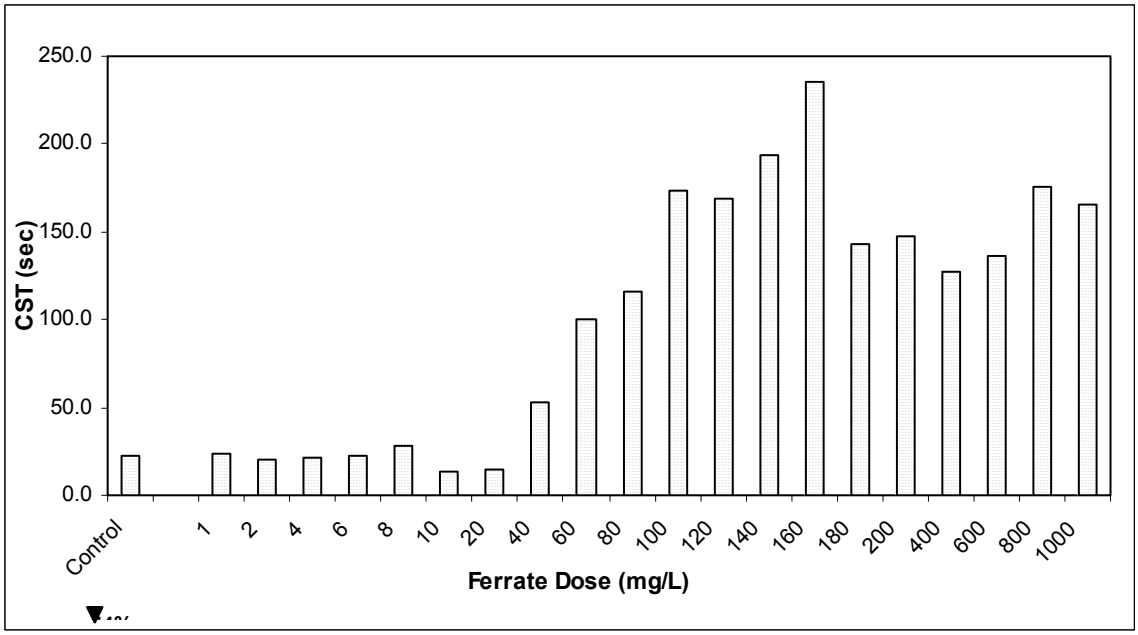


Figure 4.13 CST Times for Waste Activated Sludge Conditioned with Sodium Ferrate.

CST results indicate that an increase in CST time when the ferrate dose was increased was not only due to the insoluble ferric hydroxide species that may form at high pHs, but to some other particles that may be released from the sludge matrix when more ferrate is added to the sludge. Another possible explanation for this phenomenon is

that higher doses have higher ferric hydroxide concentrations and therefore as the dose increases the filtration is reduced. The results indicated that the optimum dose for centrifugation and filtration was 10 mg/l.

4.2.1.2 Comparison of Two Different Ferrate Products

Three different ferrate doses; 10, 100, and 1000 mg/l were used to compare dewatering effectiveness for the ferrate prepared using sodium hypochlorite and the ferrate prepared using calcium hypochlorite, which as stated previously would be called ferrate (Na^{+}) and ferrate (Ca^{+2}), respectively for proper distinction. Centrifugation and filtration were evaluated for both products. It was observed that ferrate (Ca^{+2}) provides a lower volume occupied by solids than that obtained when the ferrate(Na^{+}) was used, as illustrated in Figure 4.14. For ferrate doses of 100 and 1000 mg/l the volume occupied by solids was less for the calcium ferrate. The percent solids in the cake varied in the same way as illustrated in Figure 4.15.

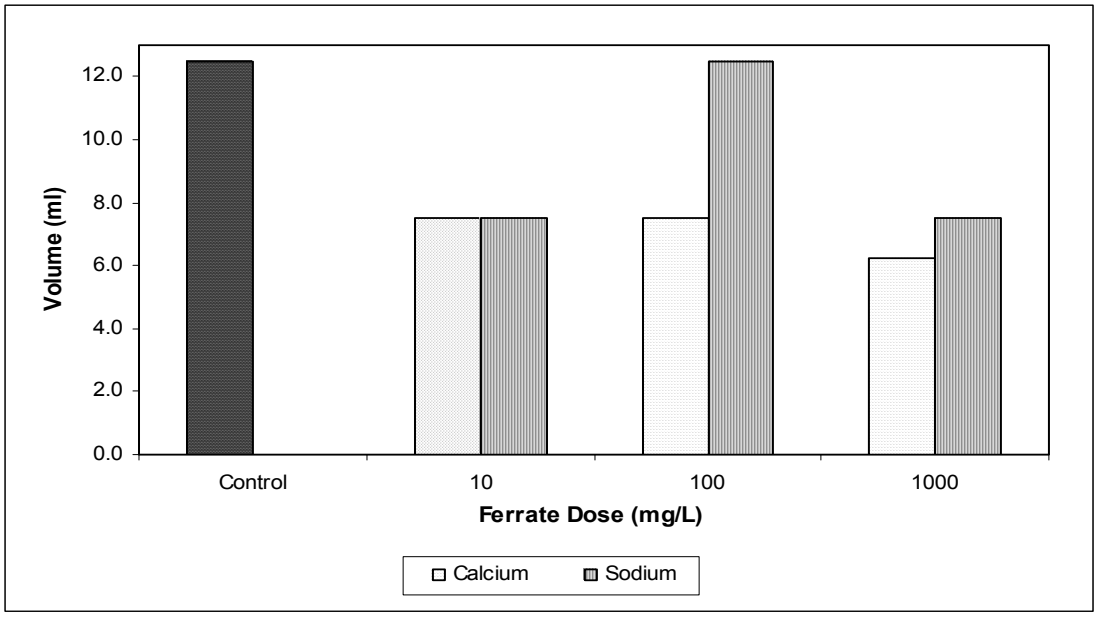


Figure 4.14 Calcium vs Sodium. Volume Occupied by Solids for Waste Activated Sludge Conditioned with Ferrate.

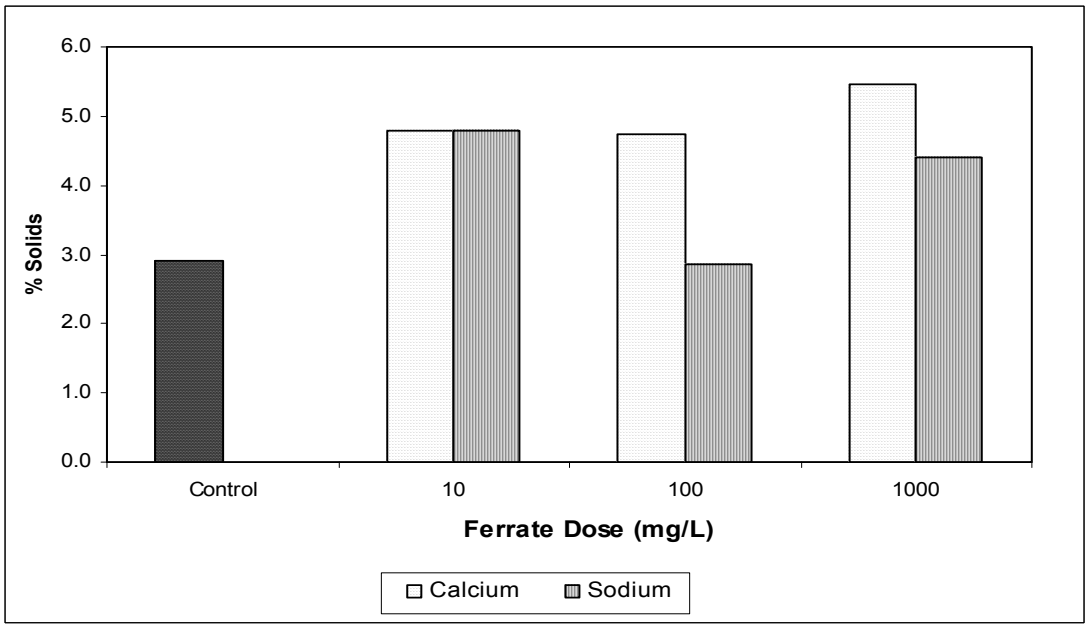


Figure 4.15 Calcium vs. Sodium. Percent of Solids in the Cake for Ferrate for Waste Activated Sludge Conditioned with Ferrate.

The turbidity of the supernatant was similar for both products when a dose of 10 mg/l was used. When doses of 100 and 1000 mg/l were used, turbidity was 69 and 25 FAU, respectively for the ferrate (Ca^{+2}), and 349 and 464 for the ferrate (Na^{+}) product as shown in Figure 4.16.

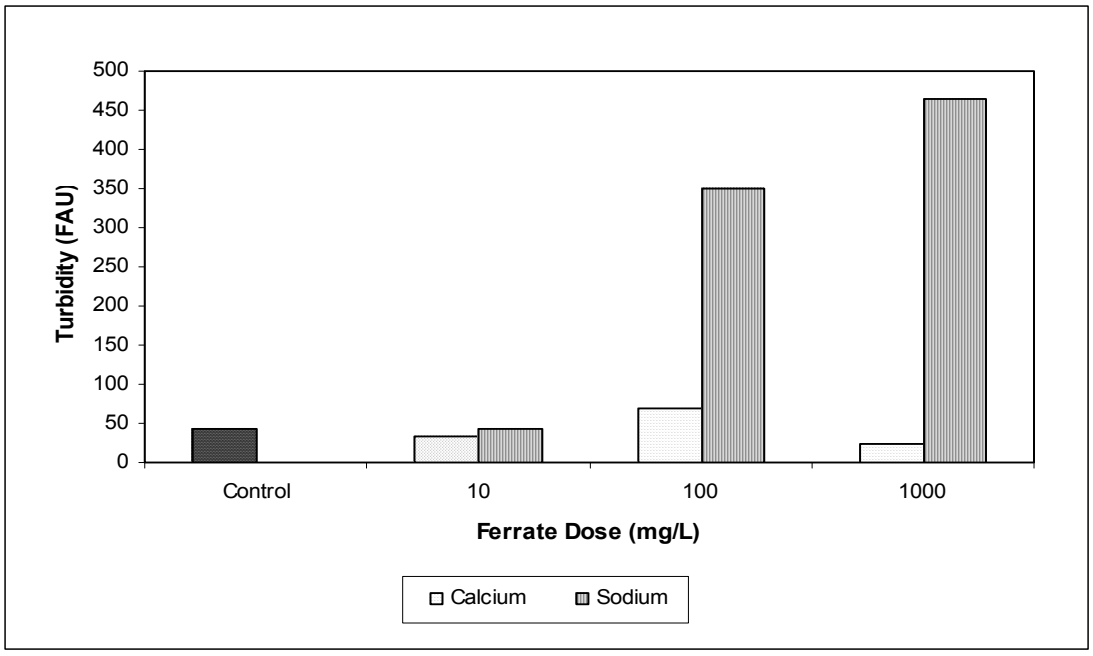


Figure 4.16 Calcium vs. Sodium. Turbidity in the Supernatant after Centrifugation for the Waste Activated Sludge.

These results indicate that the calcium ferrate provides greater volume reduction than the sodium ferrate. Significant reduction in the turbidity of the supernatant can be achieved when calcium is used as well.

As different researchers have suggested (Novak and Higgins 1997; Novak et. al 2003), divalent cations participate in bridging of negatively charge sites on the biopolymers, increasing the floc resistance to shear. The monovalent cations (like sodium) deteriorate and reduce the strength of the bonds which leads to a loss of structure and release of some of the material present on the sludge matrix. This phenomenon may be a reason for better results when calcium ferrate is used for centrifugation. The reduction in turbidity can also be attributed to the action of the divalent calcium on the reduction of the thickness of the film due to the double layer compression effect (Bruss et al. 1992; Novak and Haugan 1978; Novak and Higgins 1997; Zita and Hermansson 1994). On the other hand, when the sodium product is used some sodium chloride is also added to the biosolids because it is produced as a secondary product on the ferrate production. The sodium and sodium chloride will have adverse effects when the biosolids are used in land application for agricultural purposes because due to its presence water uptake by plant roots is limited because of the high osmotic potential (Lamsal et al. 1999). Therefore, the calcium product has more potential as a conditioning agent.

The CST results also indicate that a 60% reduction in the CST time compared to the control was observed when the ferrate (Ca^{+2}) was used compared with 41% for the ferrate (Na^{+}). These results again suggest that the calcium enhances the dewaterability properties of the waste activated sludge, as shown in Figure 4.17.

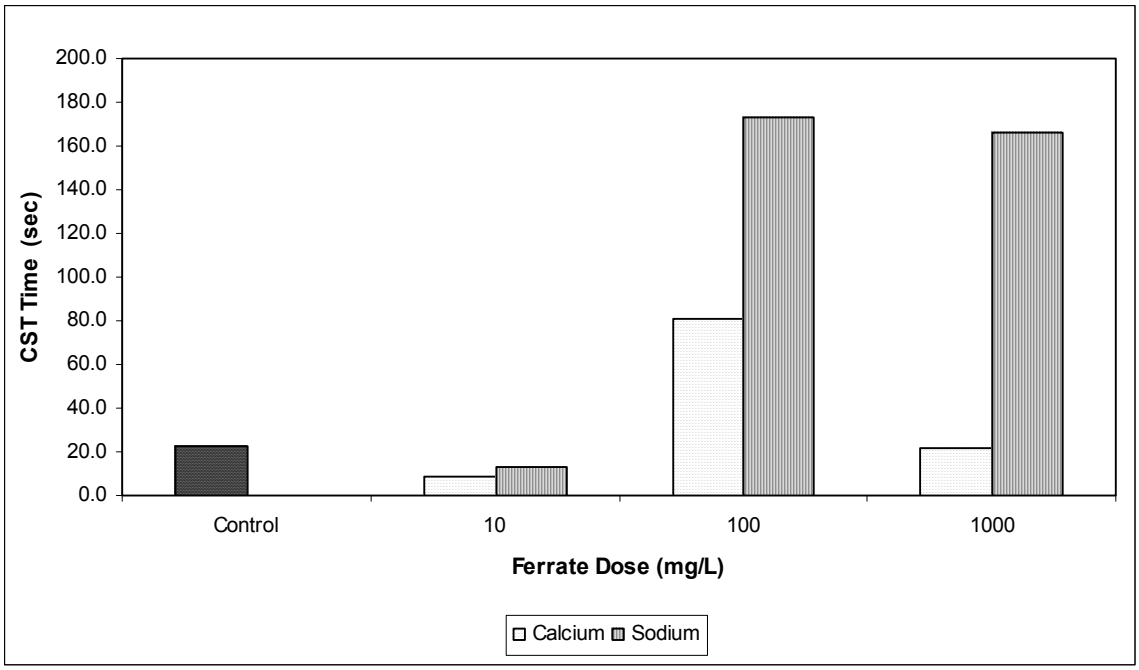


Figure 4.17 Calcium vs. Sodium. CST Times for Waste Activated Sludge Conditioned with Ferrate.

4.2.1.3 Ferrate vs. Ferric

Experiments were conducted to evaluate the dewaterability properties of each type of sludge when using ferrate vs ferric conditioners. In this case, ferric chloride and ferric chloride with lime were used as conditioners. The main purpose of these experiments was to evaluate which source of iron was more effective for dewatering. Centrifugation and filtration were evaluated for three different ferric doses; 4.7, 47, and 470 mg/l as Fe. The results presented in Figure 4.18 and Figure 4.19 show that for all

ferrate doses, higher reduction in the volume occupied by solids were achieved when ferrate is used as the conditioning agent. Apparently, the ferric produced from ferrate is a better coagulant agent than the ferric added directly.

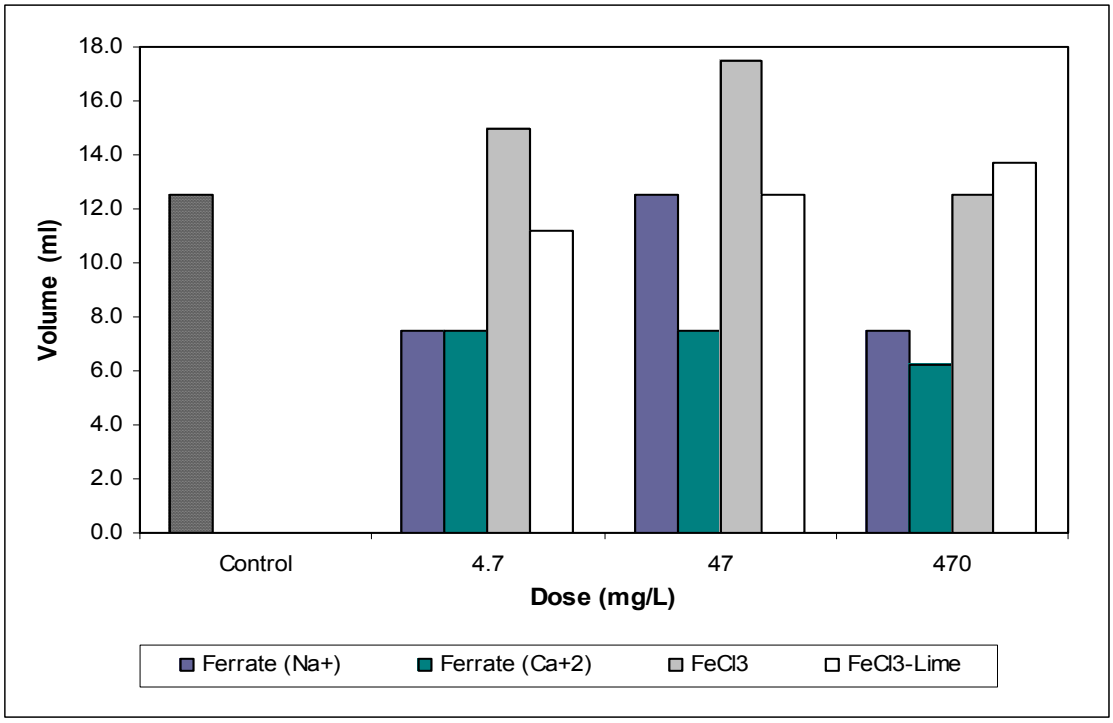


Figure 4.18 Volume Occupied by Solids for Waste Activated Sludge Conditioned with Different Doses of Ferrate and Ferric Chloride.

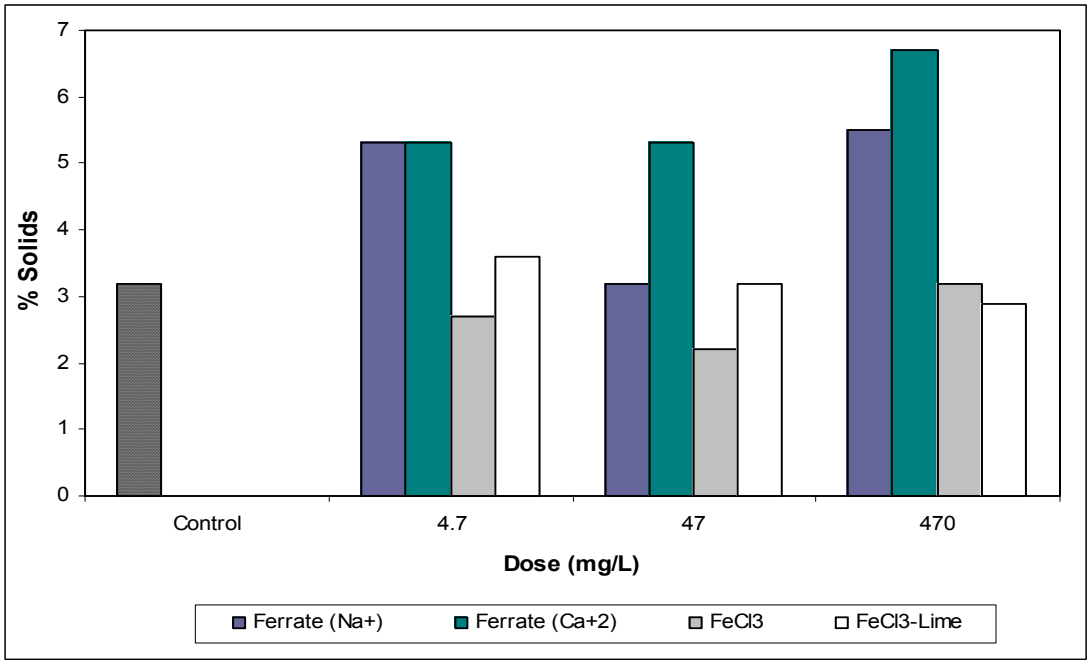


Figure 4.19 Percent of Solids in the Cake for Ferrate for Waste Activated Sludge Conditioned with Different doses of Ferrate and Ferric Chloride.

The ferrate (Ca^{+2}) offers the highest volume reduction for the sludge when centrifugation is used as a mechanical dewatering aid. However the lowest values of turbidity were achieved for ferric chloride as it is illustrated in Figure 4.20.

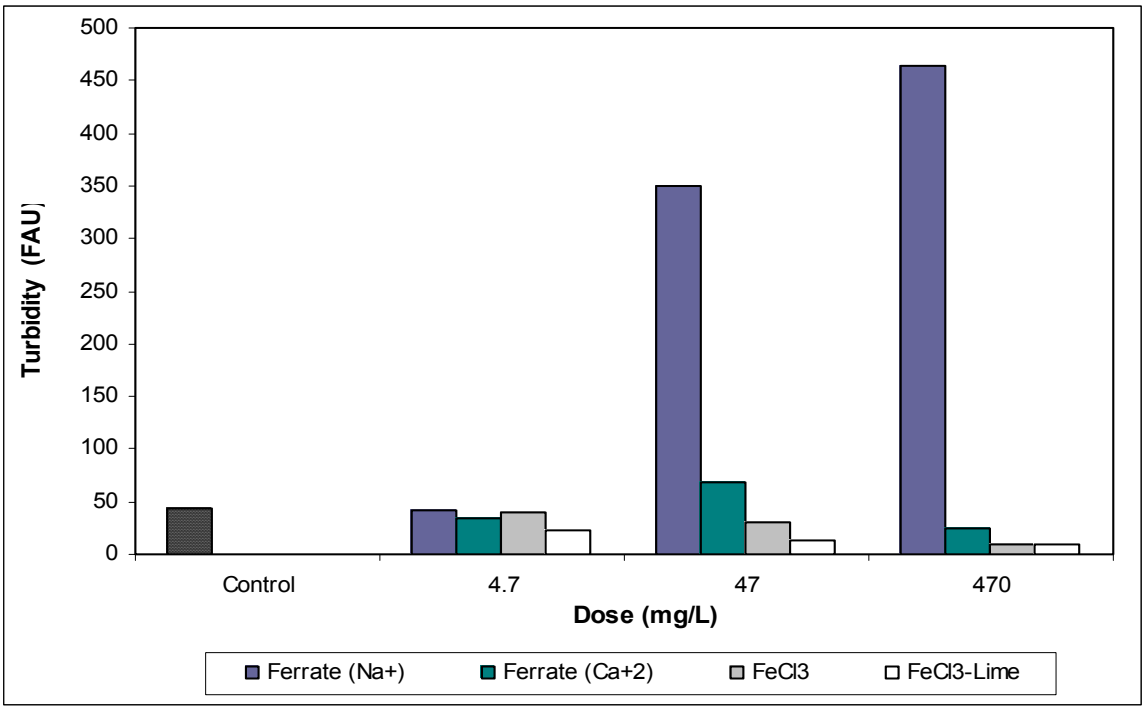


Figure 4.20 Turbidity of the Supernatant after Centrifugation of Waste Activated Sludge Conditioned Using Different Doses of Ferrate and Ferric Chloride.

A possible explanation for the high turbidity when ferrate is used may be the fact that ferrate is a strong oxidant and its addition causes the breakdown of some of the organics that are present small particles which may be suspended in the supernatant. If biopolymers degrade, material inside the sludge matrix maybe released causing an increase in turbidity.

From the CST tests it was observed that for both ferrate products the lowest CST values were obtained when the smallest dose was used (4.7 mg/l), while for the ferric chloride the lowest CST was obtained for the highest dose (470 mg/l). These results

confirm that when ferrate is added to the sludge it enhances the release of some material from the sludge matrix. Therefore, when the dose increases, the filtration time increases because there are more particles present that may clog the filter. When ferric chloride is used, it only acts as a coagulant and does not cause the release of any particles from the sludge or degradation of any organic substances. Thus, when the dose is increased the filtration time is reduced and no particles clog the filter. These results are illustrated in Figure 4.21. For centrifugation and filtration the addition of lime to ferric chloride improves the dewaterability of the sludge when doses of 4.7 and 47 mg/l were used. However, when a dose of 470 mg/l was used a slightly detrimental effect was observed with the addition of lime for centrifugation and filtration.

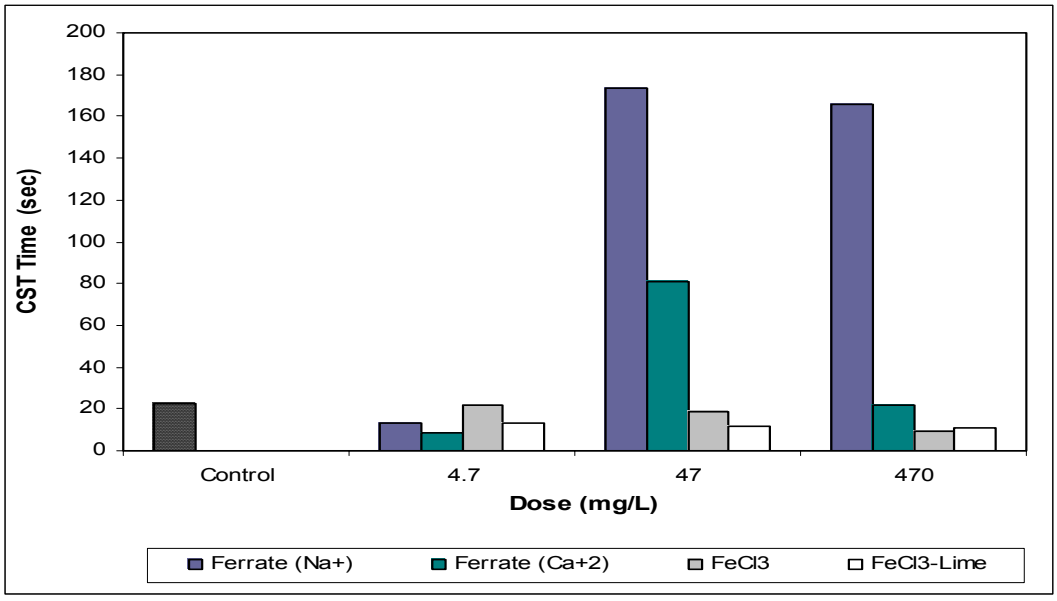


Figure 4.21 CST Times for Waste Activated Sludge Conditioned with Different Doses of Ferrate and Ferric Chloride.

4.2.1.4 Ferrate vs. Polymer

Polymers are large water-soluble organic molecules consisting of repeated chemical units joined together in chains. These large molecules contain ionized groups that form interparticle bridges with the sludge particles producing large flocs. Thus, they are used to condition the sludge prior to dewatering. Depending upon the electrical charge of the ionized groups polymers are categorized as anionic, cationic, or nonionic. Polymers may be purchased in dry form, as emulsions or as liquids. They have a typical shelf life of one year or more. Thus, these chemicals are commonly used as conditioners prior to dewatering because of ease in handling and storage, and their chemical properties (Mc Farland 2000). The effectiveness of the cationic Zetag 7848 polymer dose (0.05 mg/l) currently used at the Easter Water Reclamation Facility where the waste activated sludge samples were collected was compared with the optimum doses of each of the ferrate products used in this study at optimum pH.

The centrifugation results indicate that the optimum doses for each of the ferrate products were more effective than the polymer dose of 0.05 mg/l as shown in Figure 4.22 and Figure 4.23. The minimum volume attained when the ferrate products were used was 7.5 ml compared to 10 ml for the polymer, indicating that the most effective coagulant was the ferrate. It was also found that the turbidity of the supernatant obtained when the ferrate (Na^{+}) was used was 34% less compare to 58 FAU for the control, and 57% less for the (Ca^{+2}) as shown in Figure 4.24.

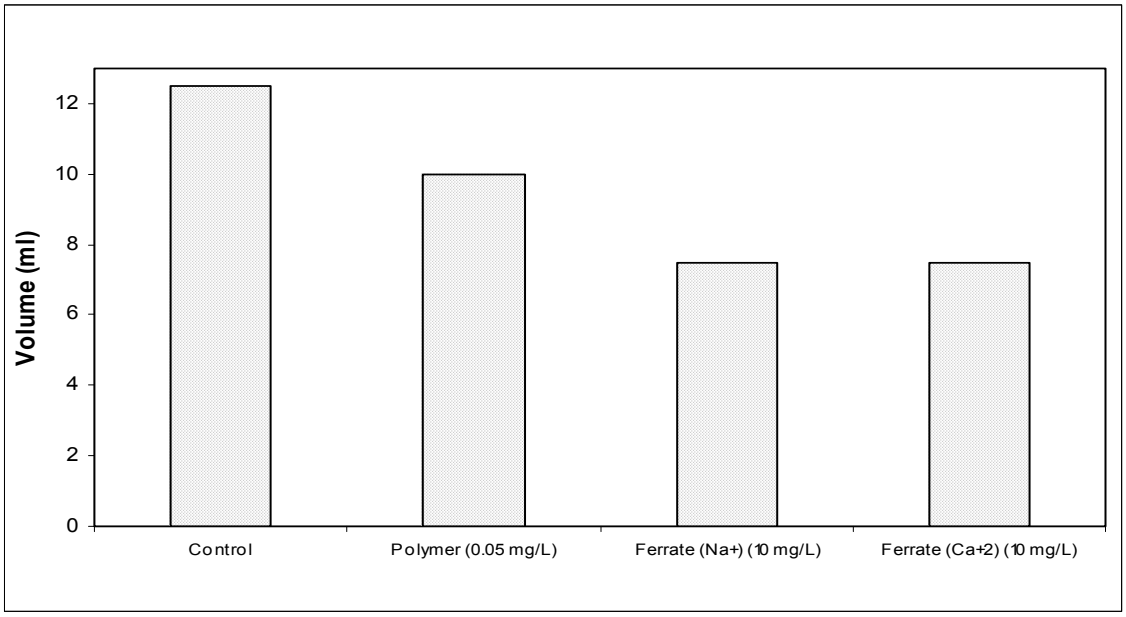


Figure 4.22 Volume Occupied by Solids for Waste Activated Sludge Conditioned with Ferrate and Polymer

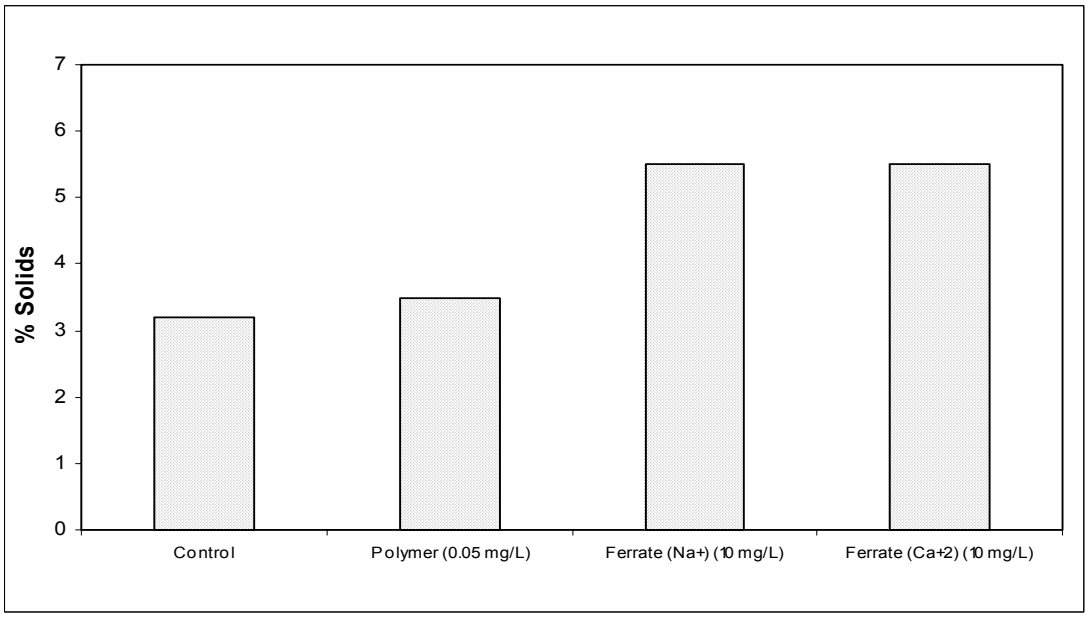


Figure 4.23 Percent of Solids on the Cake for Ferrate for Waste Activated Sludge Conditioned with Conditioned with Ferrate and Polymer.

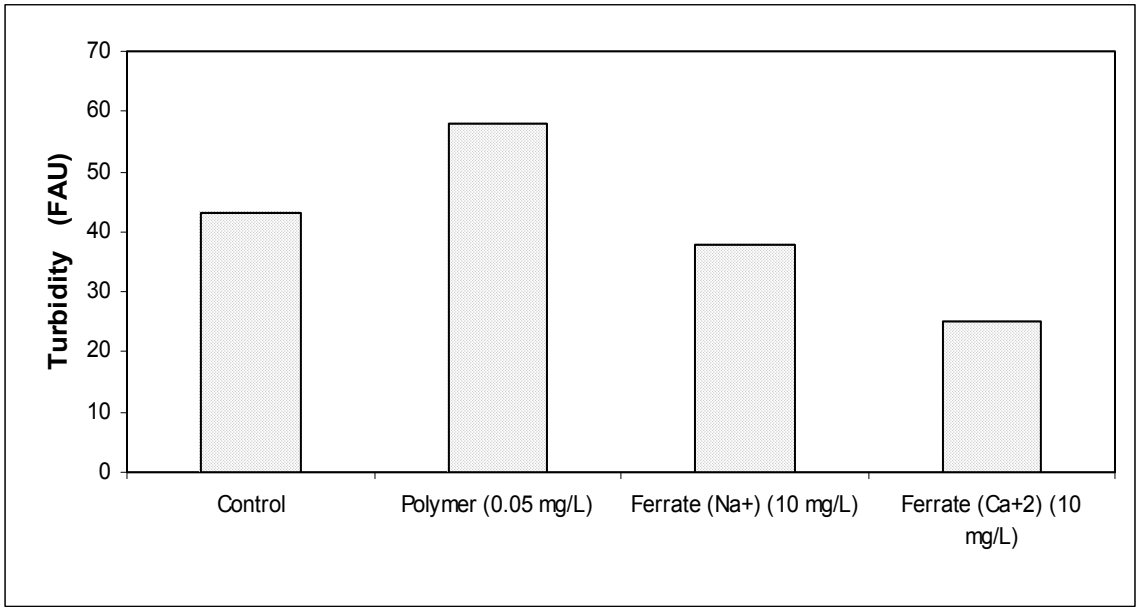


Figure 4.24 Turbidity of the Supernatant after Centrifugation for Waste Activated Sludge Conditioned with Ferrate and Polymer.

The CST results presented in Figure 4.25 indicate also that the dose of ferrate prepared with calcium was more effective than the polymer dose. The CST provided a maximum reduction of 62% when the ferrate (Ca^{+2}) is used compared to 54% reduction achieved when the polymer is used. On the other hand, the sodium ferrate reduces the CST time for the sludge by 42%, but does not offer a higher reduction than that achieved with the polymer. Once more the results suggest that the sodium cation reduces the strength of the floc producing poorer filtration results than those obtained when calcium was used, and that the ferrate (Ca^{+2}) product is best.

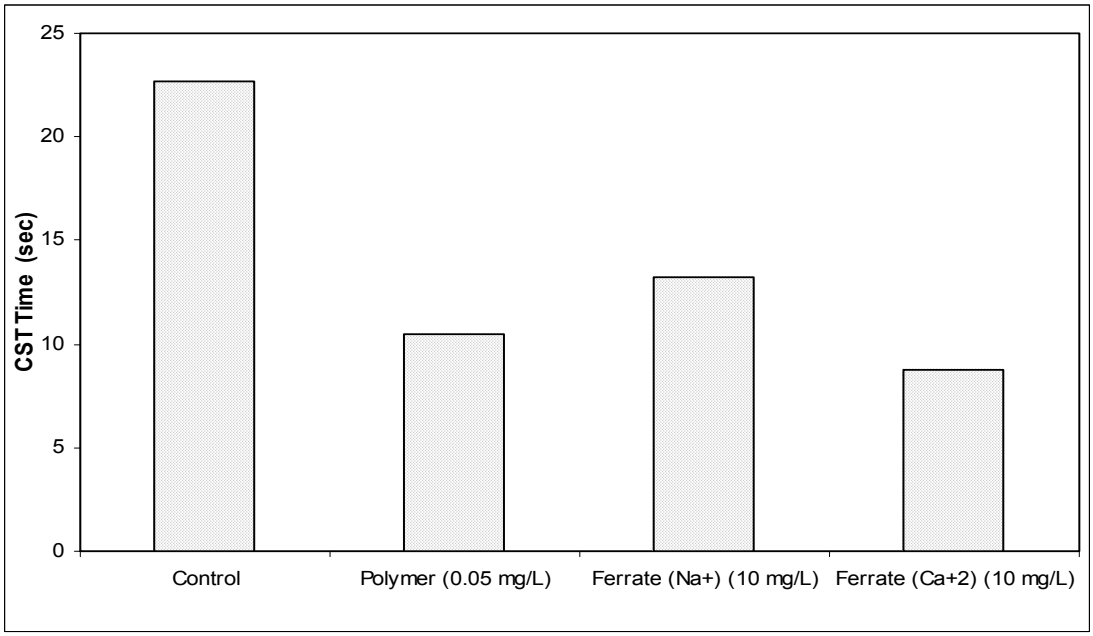


Figure 4.25 CST Times for Waste Activated Sludge Conditioned with Ferrate and Polymer

4.2.1.5 Ferrate and Polymer

As mentioned before, polymers are commonly used as conditioners prior to dewatering. However, polymers can be used only as conditioning agents, and chemical, biological or physical treatment is always required for disinfection of the sludge prior to disposal. Ferrate instead can simultaneously achieve dewatering and disinfection when the correct dose is added. When disinfection is an alternative biosolids Class A or Class B can be produced. This classification is based on the pathogen reduction. The pathogen reduction requirements for these two types of biosolids are presented in Appendix B.

Additional experiments were conducted to evaluate the alternative of using ferrate

and polymer together to achieve dewatering and disinfection in a single dosing and mixing unit process, and to reduce the polymer dose and cost for sludge treatment. For these experiments two different ferrate doses were used; a ferrate dose of 60 mg/l to achieve the pathogen reduction required for biosolids Class B and a potential ferrate dose of 119 mg/l to achieve pathogen reduction for biosolids Class A. Both doses were used in combination with different doses of cationic Zetag 7848 polymer ranging from 0.008 to 0.05mg/l (the polymer range used by the wastewater treatment plant). These experiments were conducted using the optimum conditions for rotational speed (800 rpm), pH 7.0 and no pH adjustment. Both ferrate products were tested.

For the ferrate dose of 119 mg/l used to achieve biosolids class A the centrifugation results indicated that for both ferrate products the best results were obtained when the ferrate dose was combined with a polymer dose of 0.02 mg/l at a pH 7.0. In both cases the volume occupied by solids was 5 ml compared to 12.5 ml for the control and 11.25 for the polymer control. The results are illustrated in Figure 4.26. A solids content of 6.5% was achieved in both cases. Solids of 2.9 % and 3.2% were observed for the control and the polymer control, respectively, as shown in Figure 4.27.

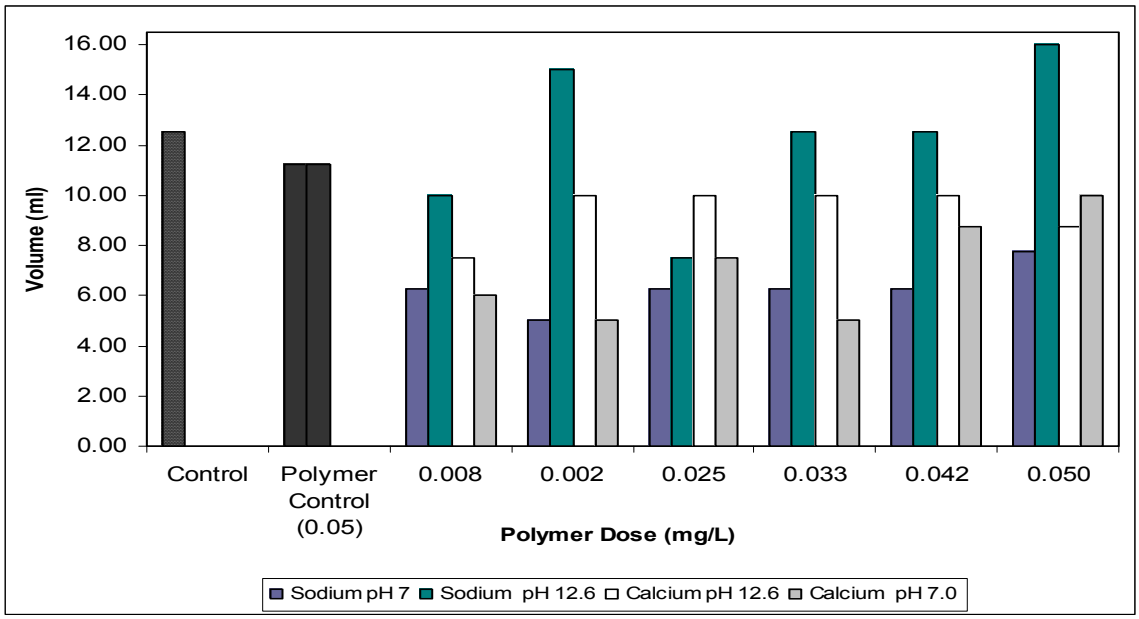


Figure 4.26 Volume Occupied by Solids for Waste Activated Sludge Conditioned with a Combination of Ferrate and Polymer (Biosolids Class A)

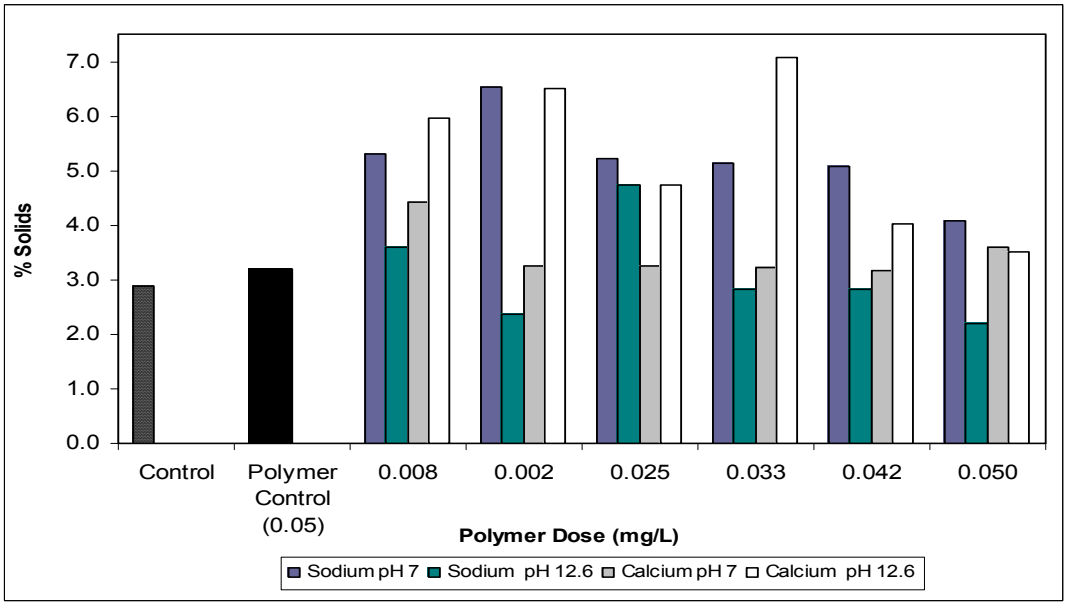


Figure 4.27 Percent Solids on the cake for Waste Activated Sludge Conditioned with a combination of Ferrate and Polymer (Biosolids Class A)

The turbidity results shown in Figure 4.28 indicate that the lowest turbidity was observed when only the polymer was used and the second lowest turbidity was observed for a combination of the ferrate (Ca^{+2}) and a polymer dose of 0.033 mg/l at pH 7.0. The optimum results for ferrate and polymer were obtained for ferrate (ca+2) at pH 7.0.

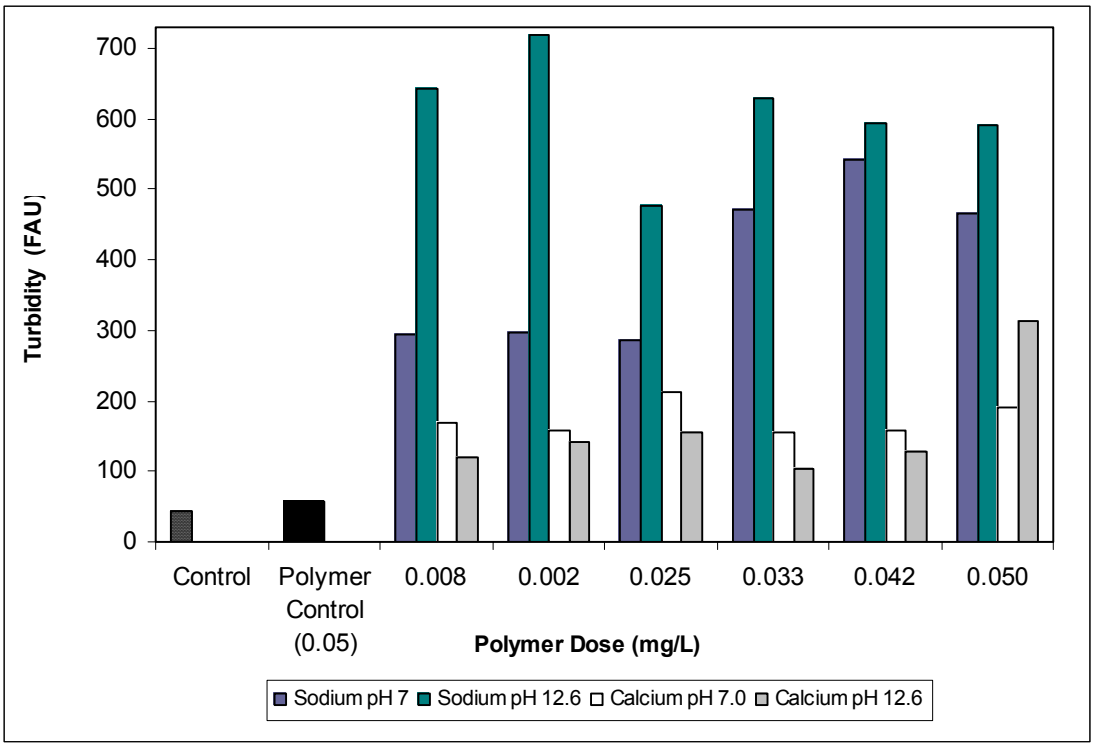


Figure 4.28 Turbidity of the Supernatant after Centrifugation of Waste Activated Sludge with a combination of Ferrate and Polymer (Biosolids Class A)

The results for the CST experiments indicate that the lowest times were obtained for the calcium ferrate and a polymer dose of 0.02 mg/l at pH 7.0. However, none of the ferrate-polymer combinations provided a CST lower than that obtained for the polymer alone, which indicates that a combination of polymer and ferrate does not enhance the dewaterability of the sludge when filtration is used, as shown in Figure 4.29. This phenomenon may have occurred because the ferrate, which is a strong oxidant, reacted with the organic polymer, breaking its long chains and reducing the possibility of forming large flocs, and therefore deteriorating the dewatering properties of the sludge. At high pH, higher CST times were observed for both ferrate products. This phenomenon could be caused by the release of particles from the sludge matrix as explained before or because the pH range at which the polymer works best is between 6 and 7.5 (based on the information provided by Fort Bend Services, Inc)

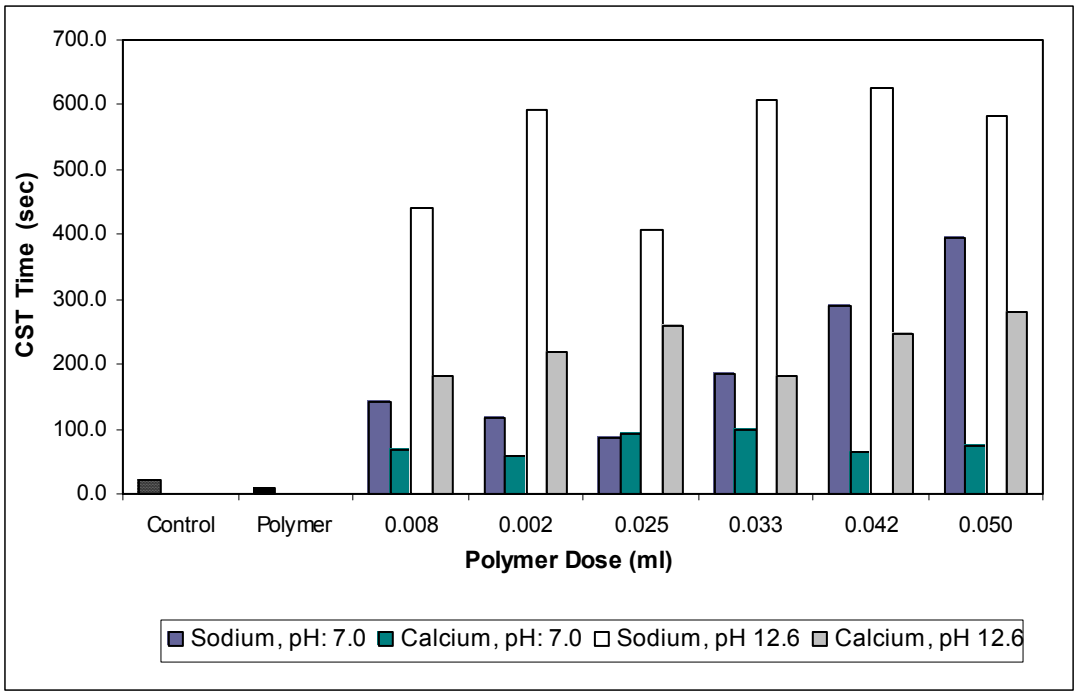


Figure 4.29 CST Values for Waste Activated Sludge Conditioned with Ferrate and Polymer Simultaneously (Biosolids Class A)

The optimum results obtained for centrifugation and filtration were compared to those obtained when the ferrate alone was used at the same pH. The results show that for filtration, when polymer is combined with ferrate, a reduction in the control CST time of 28% and 49% are obtained for the calcium and the sodium ferrate products, respectively, which indicates that dewaterability is improved when the combination of polymer-ferrate is used compared with the ferrate alone. The results are shown in Figure 4.30. For centrifugation, a reduction in the volume occupied by solids was observed when the polymer was used in combination with ferrate. These reductions were 33% and 60% for the calcium and sodium products, respectively as shown in Figure 4.31. These results

indicate that a combination of polymers improves the dewaterability of the sludge compared to the results obtained for ferrate alone.

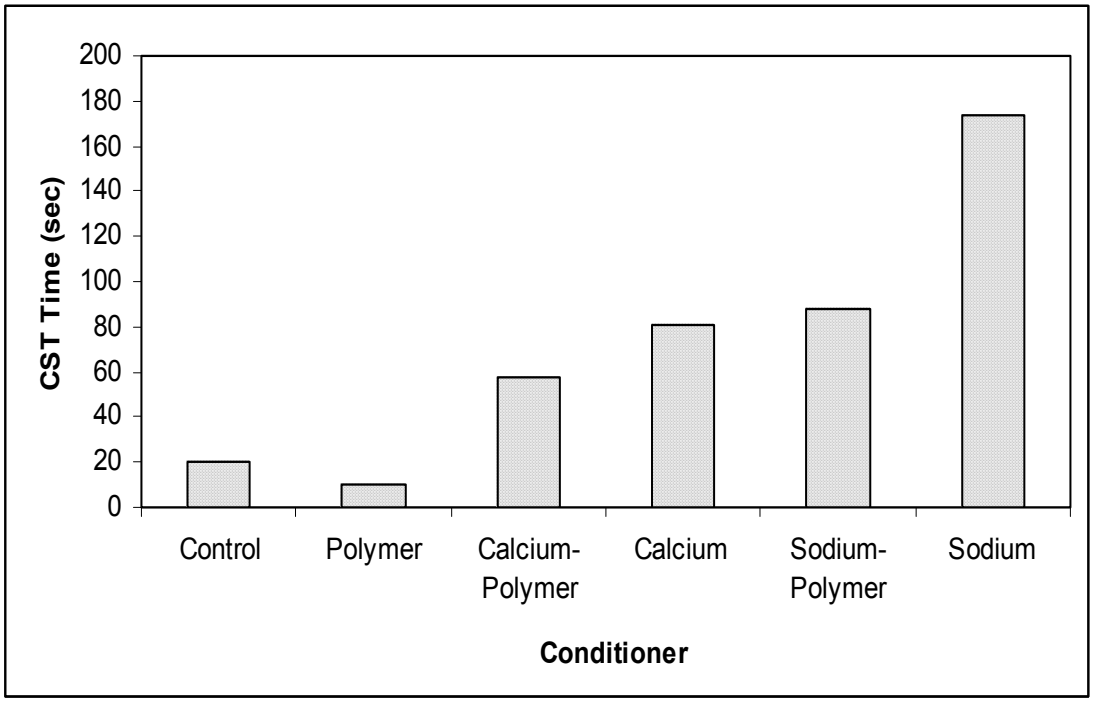


Figure 4.30 CST Values for Waste Activated Sludge Conditioned with Ferrate Alone and a Combination of Ferrate and Polymer (Biosolids Class A)

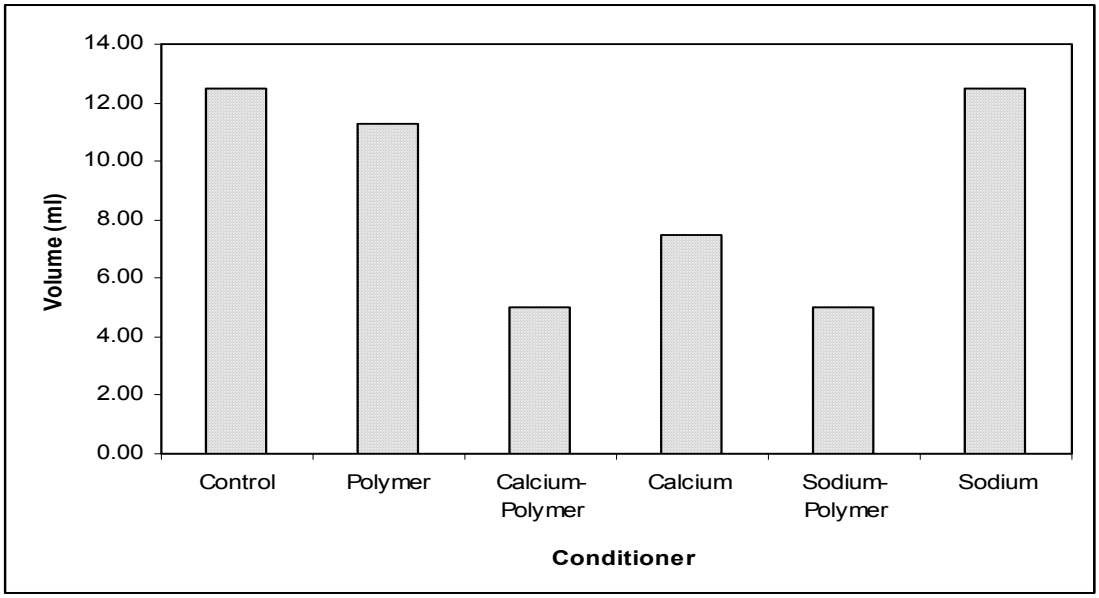


Figure 4.31 Volume Occupied by Solids for Waste Activated Sludge Conditioned with Ferrate Alone and a Combination of Ferrate and Polymer (Biosolids Class A)

For the ferrate dose of 60 mg/l used to achieve biosolids class B the centrifugation results indicated that both ferrate products combined with a polymer dose of 0.02 mg/l offered the highest reduction in the volume occupied by the solids at pH 7.0. For the ferrate (Na^{+}) the volume of occupied by solids was 4.25 ml, compared to 12.5 ml for the control, and 11.25 for the polymer alone (0.05 mg/l). For the ferrate (Ca^{+2}) the volume occupied by solids was 5.0 ml, compared to 12.5 ml for the control, and 11.25 for the polymer alone (0.05 mg/l). The results are illustrated in Figure 4.32. A solids content of 7.5 % and 7.1% was achieved for the combination of polymer and ferrate (Na^{+}) and polymer and ferrate (Ca^{+2}), respectively (both at pH 7.0). Solids of 2.9 % and 3.2% were observed for the control and the polymer control, respectively, as shown in Figure 4.33.

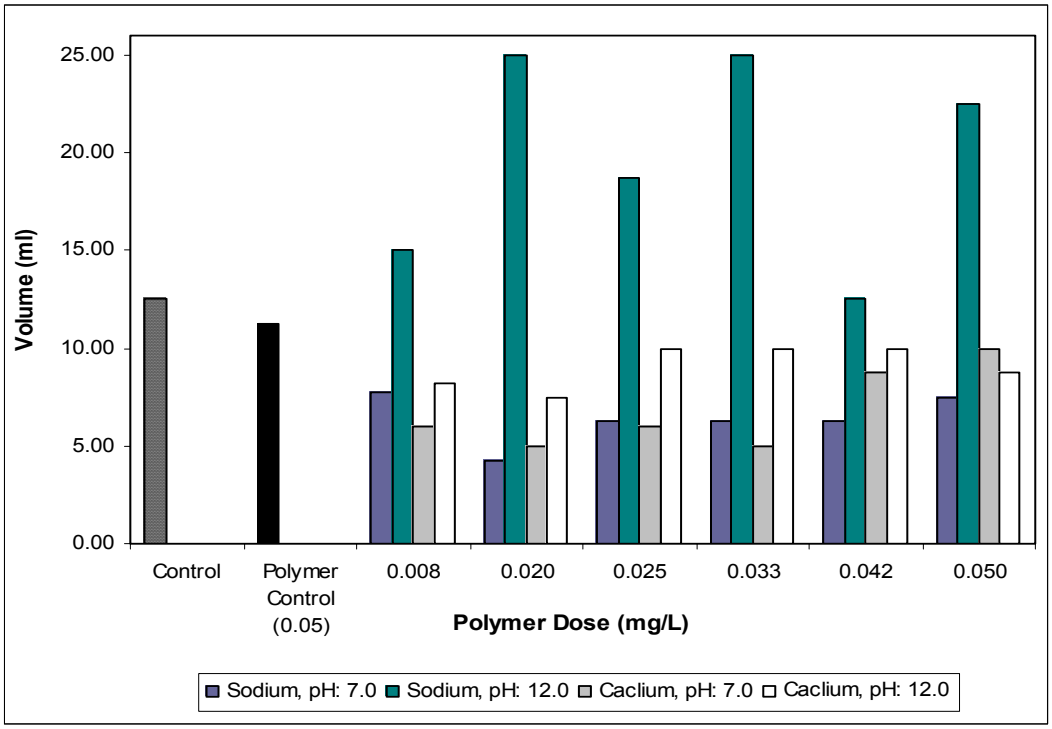


Figure 4.32Volume Occupied by Solids for Waste Activated Sludge Conditioned with a Combination of a Ferrate and Polymer (Biosolids Class B)

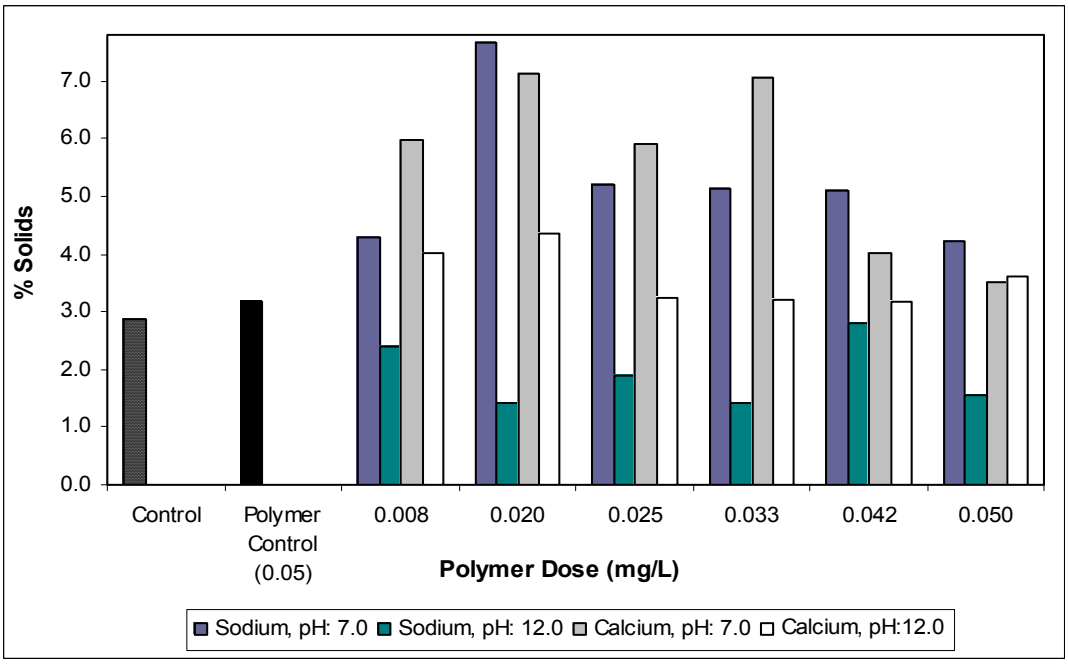


Figure 4.33 Percent Solids on the Cake for Waste Activated Sludge Conditioned with a Combination of Ferrate and Polymer (Biosolids Class B)

The turbidity results shown in figure 4.34 indicate that the lowest turbidity was observed when the ferrate (Ca^{+2}) combined with a dose of 0.02 mg/l of polymer was used providing 11.6% reduction in turbidity compared to 43 FAU for the control, and 34% reduction in turbidity compared to 58 FAU for the polymer alone (0.05 mg/l).

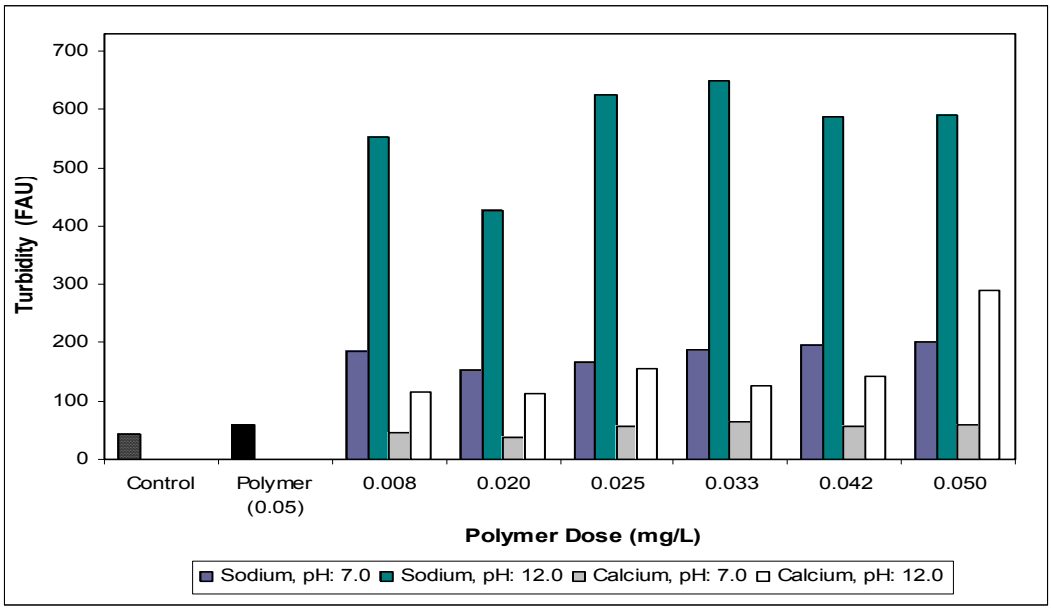


Figure 4.34 Turbidity of the Supernatant after Centrifugation of Waste Activated Sludge with a Combination of Ferrate and Polymer (Biosolids Class B)

The results for the CST experiments indicate that the lowest times were obtained for the ferrate (Ca^{+2}) and a polymer dose of 0.02 mg/l at pH 7.0. However, none of the ferrate-polymer combinations provided a CST lower than that obtained for the polymer alone, as shown in Figure 4.35. As mentioned previously this phenomenon may have occurred because the ferrate, which is a strong oxidant, reacted with the organic polymer, breaking its long chains and reducing the possibility of forming large flocs. At high pH, higher CST times were observed for both ferrate products. This phenomenon could be caused by the release of particles from the sludge matrix as explained before or because the pH range at which the polymer works best is between 6 and 7.5 (based on the information provided by Fort Bend Services, Inc).

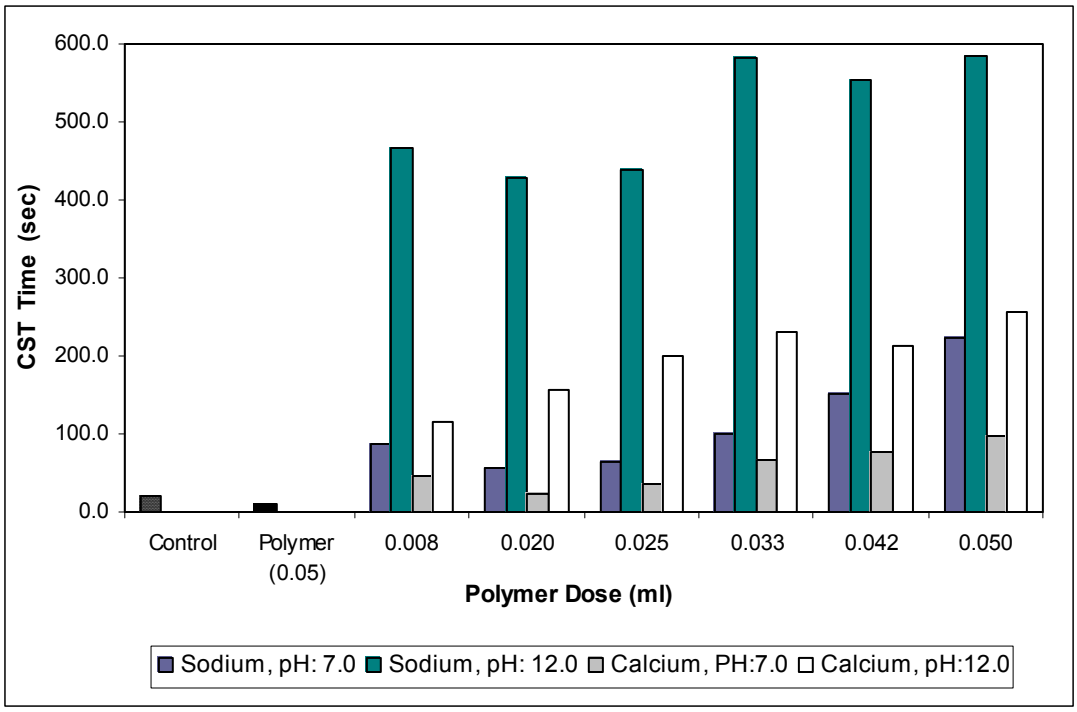


Figure 4.35CST Values for Waste Activated Sludge Conditioned with Ferrate and Polymer Simultaneously (Biosolids Class B)

The optimum results obtained for centrifugation and filtration were compared to those obtained when the ferrate alone was used at the same pH. These results show that for filtration, when polymer is combined with the disinfection ferrate dose, a reduction in CST time of 44% is obtained for the combination of polymer-ferrate (Na^{+}) compare to 100 seconds for the ferrate (Na^{+}) alone, and a 65 % reduction for the combination of polymer-ferrate (Ca^{+2}) compare to 66 seconds for the ferrate (Ca^{+2}) alone. The CST for the polymer dose of 0.02 mg/l was 23.3 seconds. These results indicate that dewaterability is improved when the combination of polymer-ferrate is used compared

with the ferrate alone. The results are shown in Figure 4.36. For centrifugation, a reduction in the volume occupied by solids was observed when the polymer was used in combination with ferrate. These reductions were 43% for the combination of polymer-ferrate (Na^{+}) compare to 7.50 ml for the ferrate (Na^{+}) alone, and a 26 % reduction for the combination of polymer-ferrate (Ca^{+2}) compare to 6.75 ml for the ferrate (Ca^{+2}) alone as shown in Figure 4.37. These results indicate that a combination of polymer-ferrate improves the dewaterability of the sludge compared to the results obtained for ferrate alone.

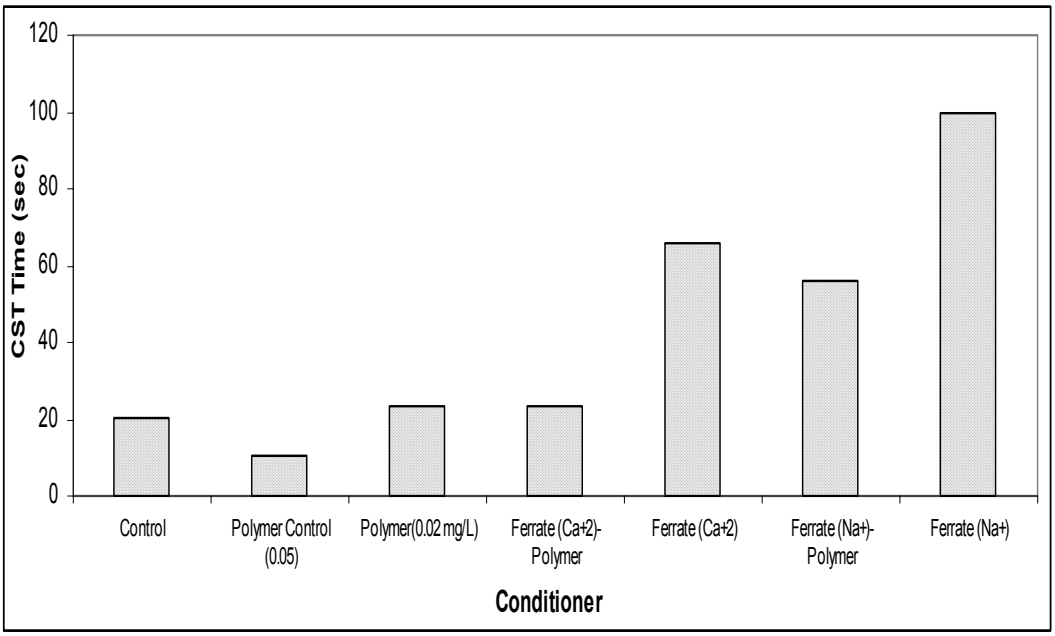


Figure 4.36 CST Values for Waste Activated Sludge Conditioned with Ferrate Alone and a Combination of Ferrate and Polymer (Biosolids Class B)

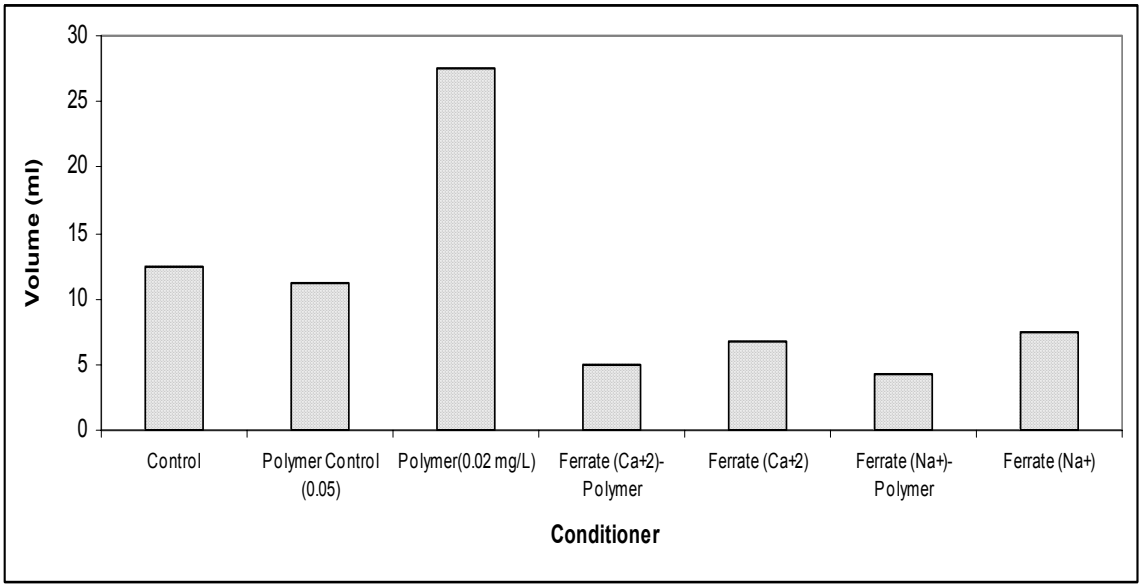


Figure 4.37 Volume Occupied by Solids for Waste Activated Sludge Conditioned with Ferrate Alone and a Combination of Ferrate and Polymer (Biosolids Class B)

4.2.2 Anaerobic Digested Sludge

4.2.2.1 Optimum Dose

Centrifugation and filtration experiments were conducted using a pH 7.0 and a rotational speed of 2400 rpm defined as the optimal conditions during the preliminary experiments, and ferrate doses ranging from 10 mg/l to 6000 mg/l, which provide a wide range. These experiments were initially conducted using ferrate prepared with sodium hypochlorite, and then compared with the results obtained for the ferrate prepared using calcium hypochlorite.

As Figure 4.38 and Figure 4.39 reveal, the optimum dose for centrifugation was

5000 mg/l, which provides a reduction in volume occupied by solids of 5 ml compared to 19 ml for the control, and a solids of 15.6% was achieved compared to solids of 4.2% for the control. The lowest turbidity was attained for the same dose as shown in Figure 4.40.

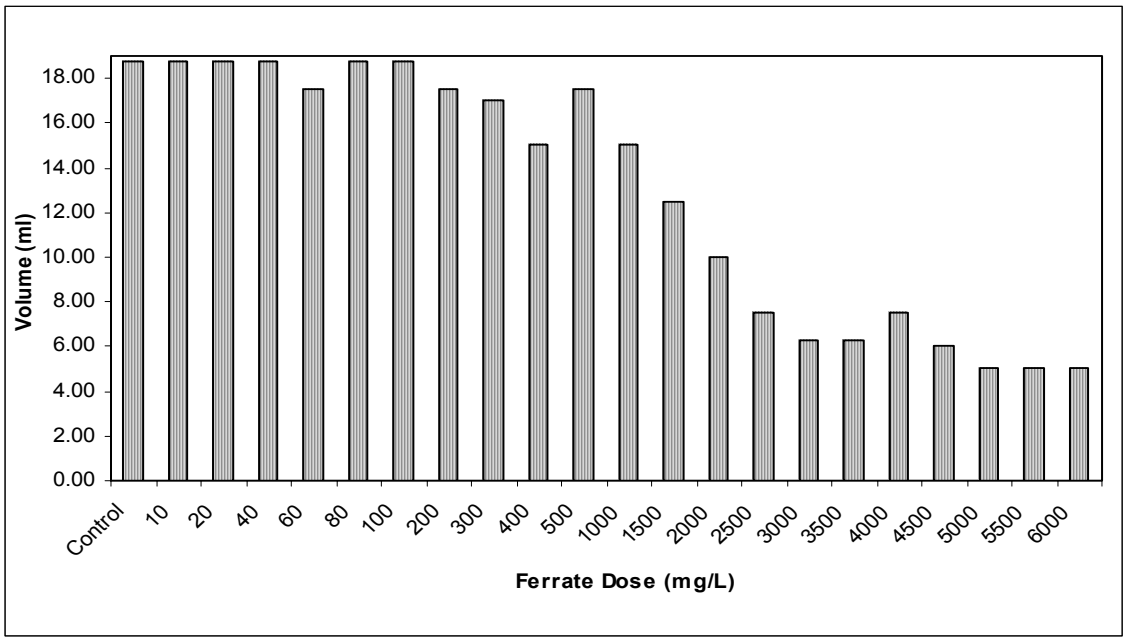


Figure 4.38 Volume Occupied by Solids for Anaerobic Digested Sludge Conditioned with Sodium Ferrate.

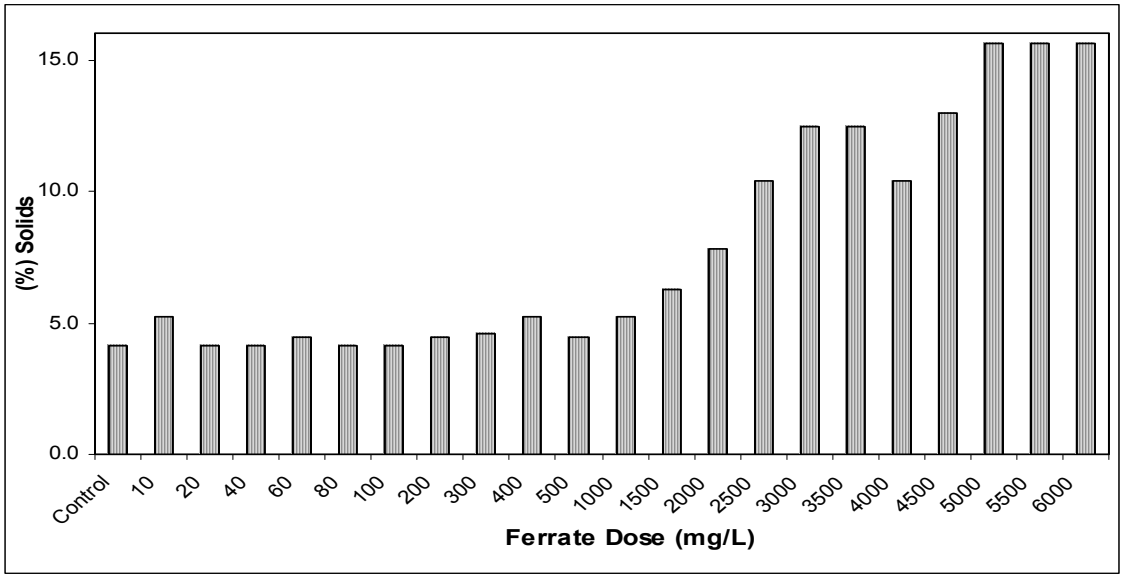


Figure 4.39 Percent Solids of the Cake for Anaerobic Digested Sludge Conditioned with Sodium Ferrate

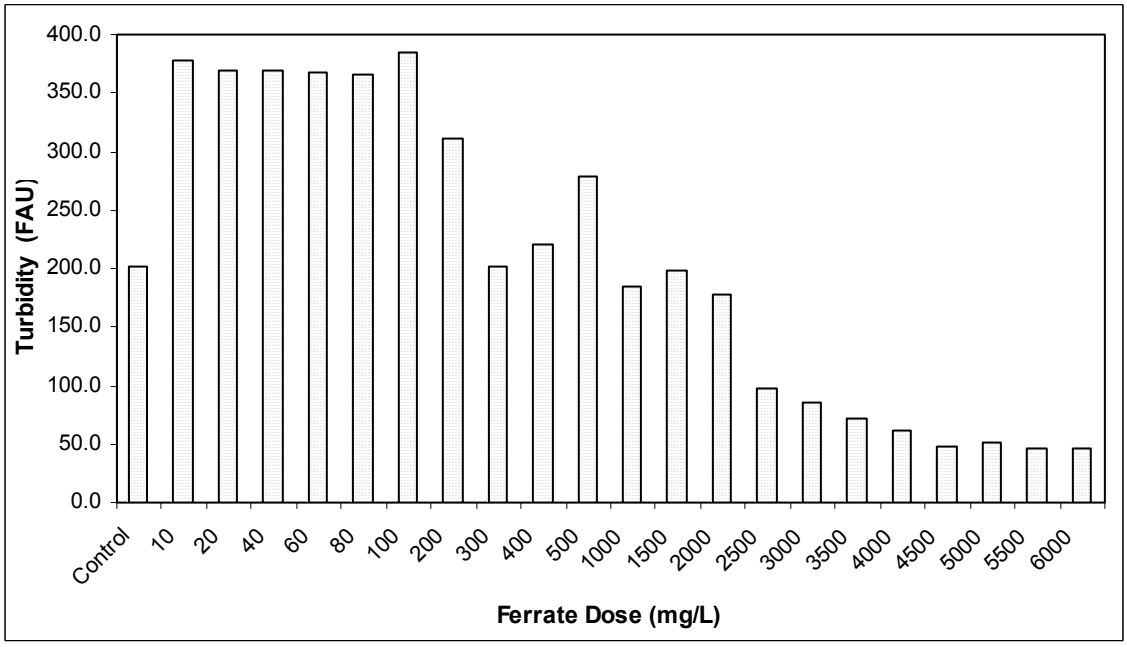


Figure 4.40 Turbidity of the Supernatant after Centrifugation for Anaerobic Digested Sludge Conditioned with Sodium Ferrate

The CST results indicated that the optimum dose for filtration was the same optimum dose for centrifugation, 5000 mg/l. This dose provides a 17% reduction in the time of filtration compared to 62.6 sec for the control. The results are presented in Figure 4.41.

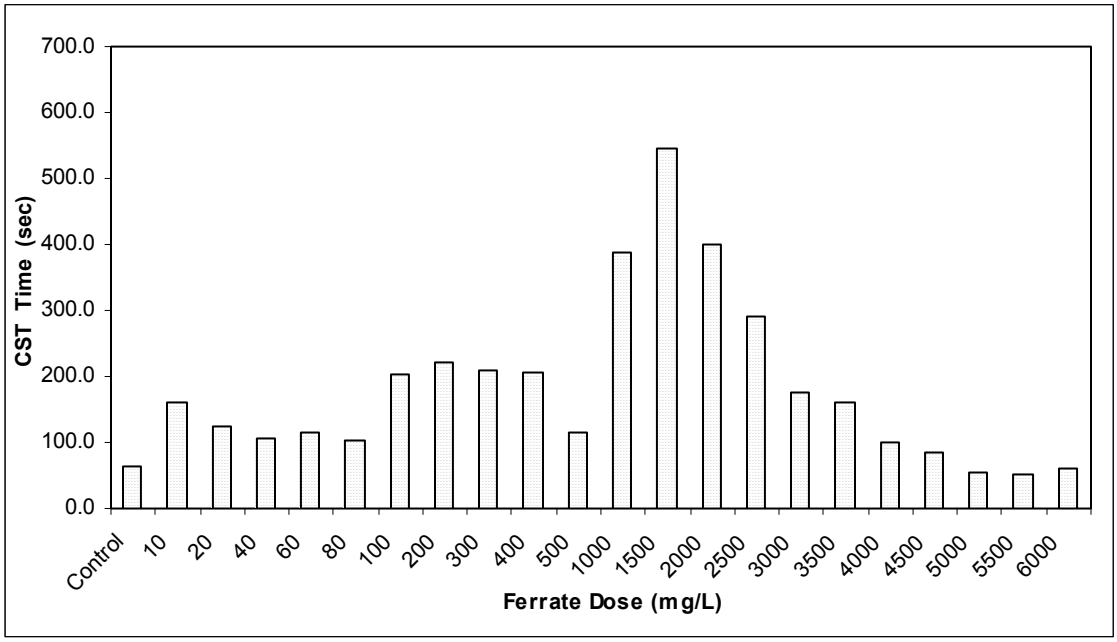


Figure 4.41 CST Times for Anaerobic Digested Sludge Conditioned with Sodium Ferrate.

For the anaerobic digested sludge the results indicate that when the ferrate dose is increased, the CST is reduced. Unlike the waste activated sludge, turbidity is created by iron particles that precipitate at high pHs and appears to be the only factor affecting the

CST when pH was not adjusted (pH= 13.8). This founding indicates that for the anaerobic digested sludge the CST results can be correlated with those obtained in the centrifugation test.

4.2.2.2 Comparison of Two Different Ferrate Products

Three different ferrate doses were used to compare dewatering effectiveness for the ferrate (Na^{+}) and the ferrate (Ca^{+2}) the calcium ferrate. Centrifugation and filtration were evaluated for both products at pH 7.0 using a rotational speed of 2400 as the optimum conditions, as defined during the preliminary experiments.

It was observed that, unlike the waste activated sludge; there was no significant difference between the results obtained for each product as illustrated in Figure 4.42. The same results are found in Figure 4.43 for the increase in the percent solids. However, the turbidity of the supernatant for the optimum dose was lower when the calcium ferrate was used. A maximum reduction in turbidity of 77% was observed for the sodium product compared to the control, while a reduction of 66% is achieved with the calcium product as shown in Figure 4.44. This founding indicates that the sodium product offered slightly better flocculating properties for the anaerobic digested sludge at this dose. For doses of 500 and 5000 mg/l the lowest turbidity was observed for the ferrate (Ca^{+2}).

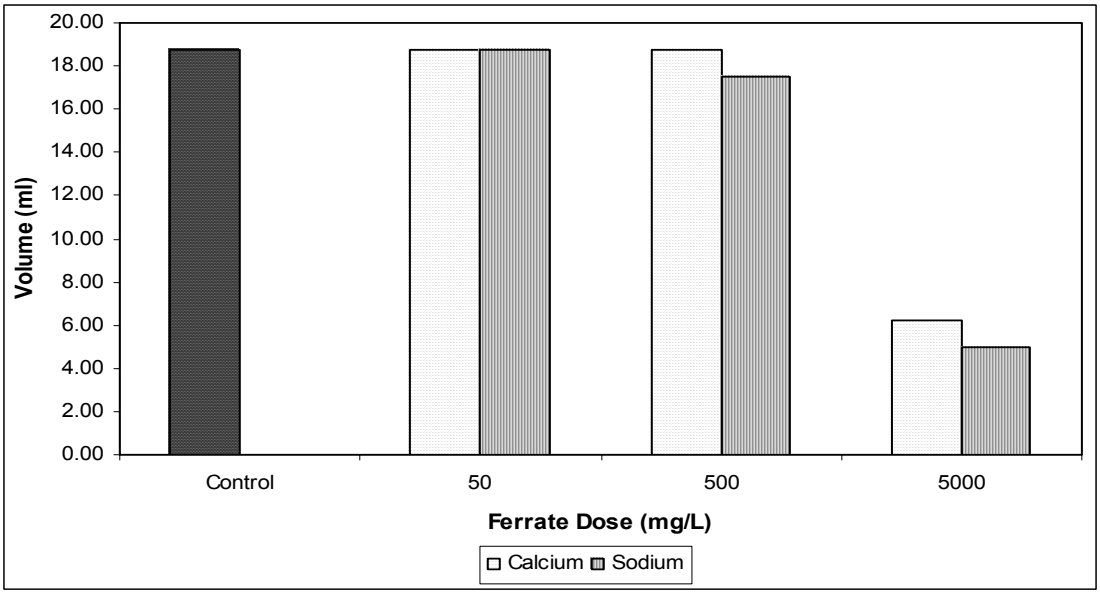


Figure 4.42 Calcium vs. Sodium. Volume Occupied by Solids for Anaerobic Digested Sludge Conditioned with Ferrate.

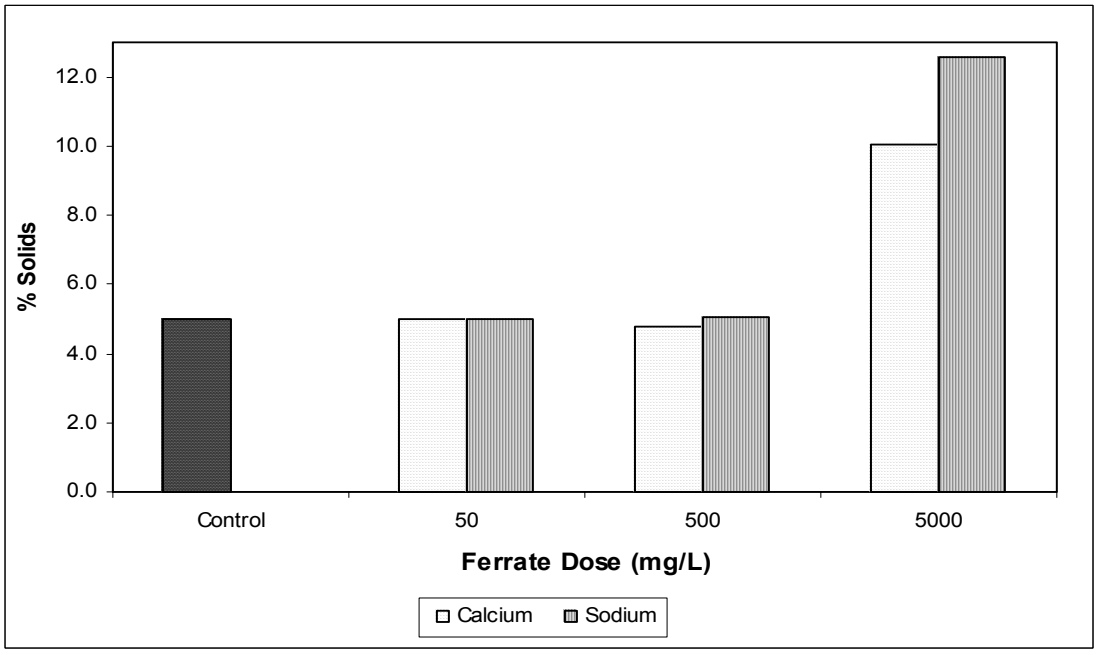


Figure 4.43 Calcium vs. Sodium. Solids on the Cake for Ferrate for Waste Activated Sludge Conditioned with Ferrate.

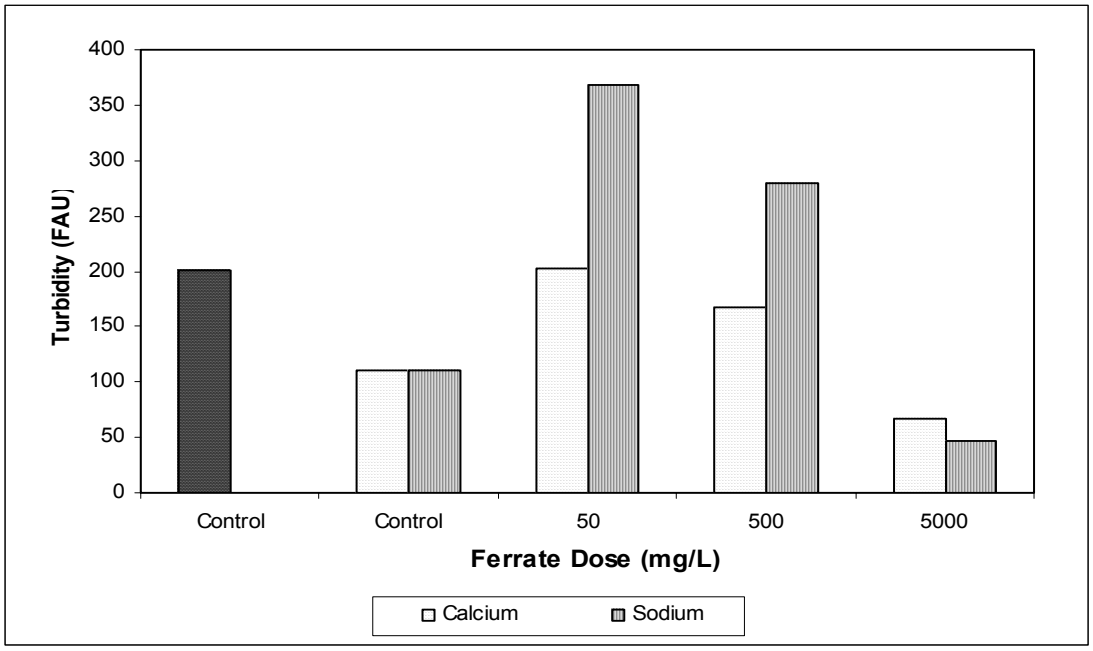


Figure 4.44 Turbidity of the Supernatant after Centrifugation for Ferrate Prepared with Calcium and Sodium for the Anaerobic Digested Sludge.

The CST results shown in Figure 4.45 indicate that a maximum 66% reduction of on the control CST (62.6 sec) when the ferrate (Na^{+}) was used, compared to 30% reduction when the ferrate (Ca^{+2}) was used. Once again the advantages of calcium over sodium observed for waste activated sludge are not seen for anaerobic digested sludge.

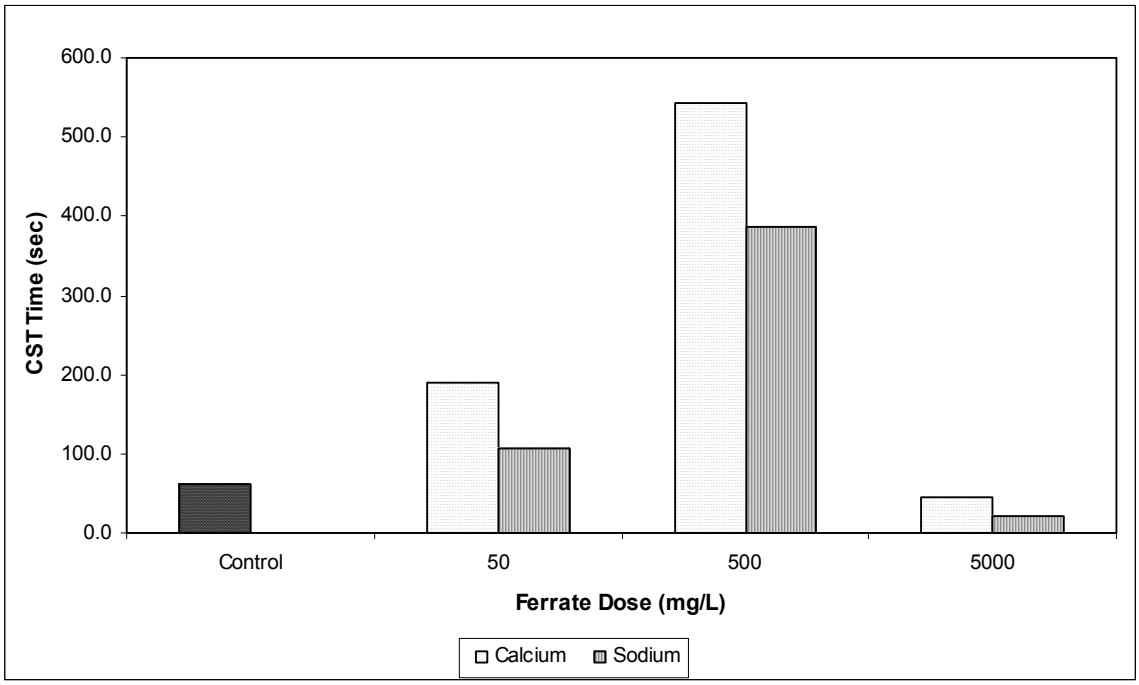


Figure 4.45 Calcium vs. Sodium. CST Times for Anaerobic Digested Sludge Conditioned with Ferrate.

4.2.2.3 Ferrate vs. Ferric

Experiments were conducted to evaluate the dewaterability properties for each type of sludge using ferrate vs. ferric conditioners at pH 7.0. In this case, ferric chloride and ferric with lime were used as conditioners. Centrifugation and filtration were evaluated for three different doses; 23, 230, and 2300 mg/l as Fe. The results presented in Figure 4.46 show that for 23 and 230 mg/l there was no significant difference in the volume reduction obtained when ferrate and ferric coagulants are used. However, when a dose of 2300 mg/l was used it was observed that the ferrate products provide higher

volume reduction than that obtained when the ferric coagulants were used. The volume occupied by solids for the ferrate products was 5 ml for the sodium ferrate and 6.25 for the calcium ferrate compared to 19 ml for the control. For the ferric coagulants the volume occupied by solid was 15 ml as shown in Figure 4.46. Similar results are observed in the percent solids of the cake in Figure 4.47.

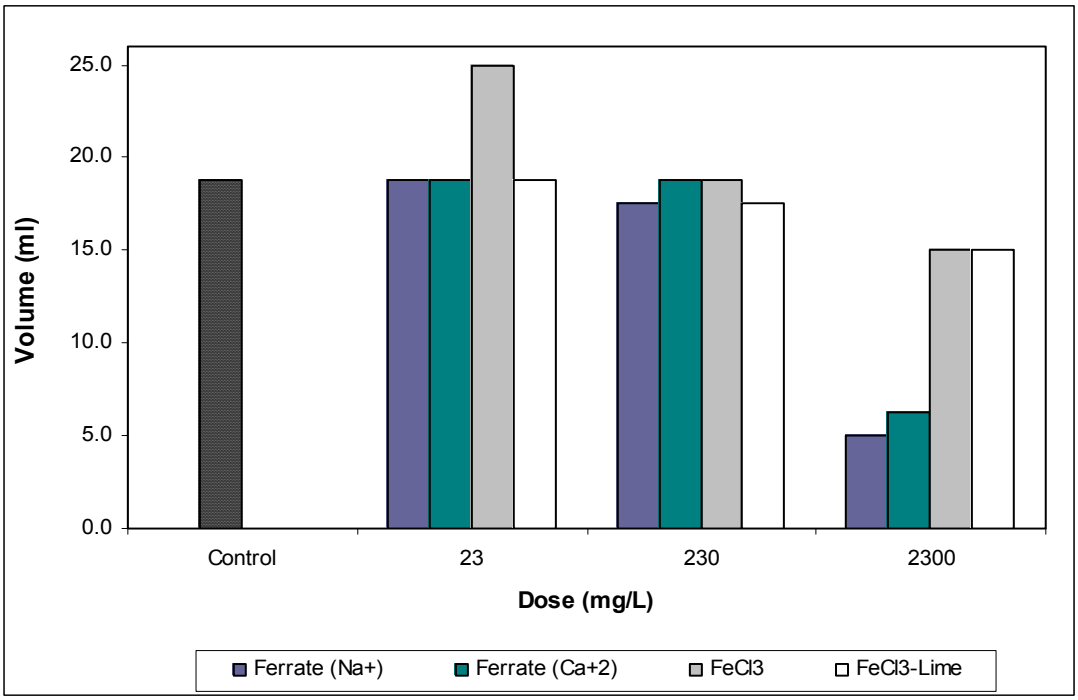


Figure 4.46 Volume Occupied by Solids for Anaerobic Digested Sludge Conditioned with Different Doses of Ferrate and Ferric Chloride.

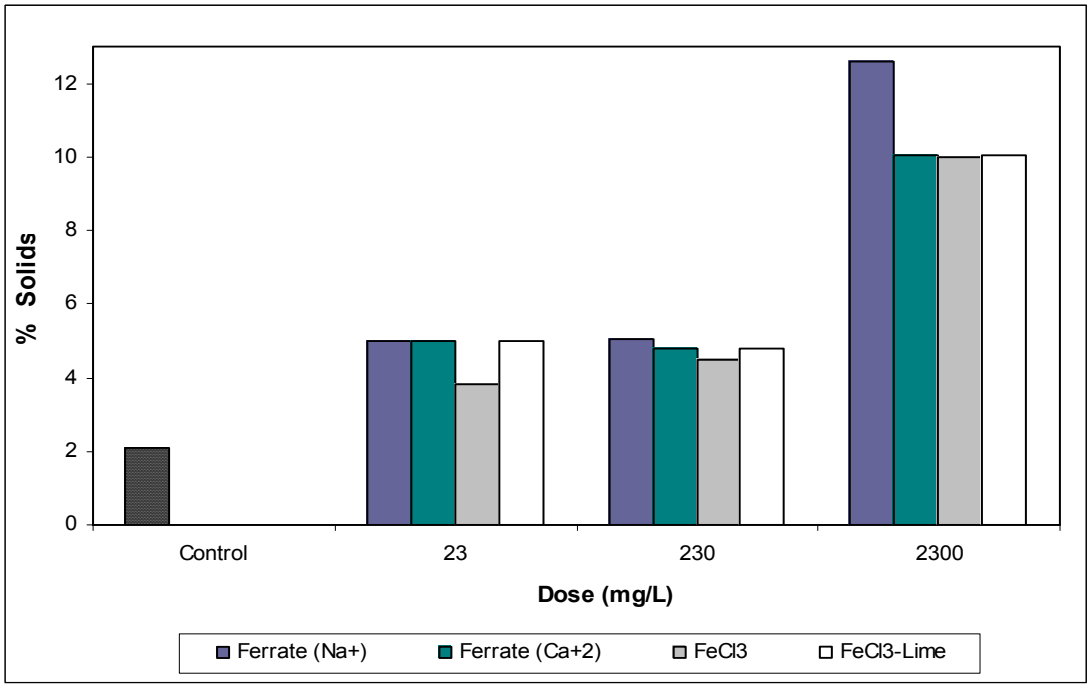


Figure 4.47 Solids for Anaerobic Digested Sludge Conditioned with Different Doses of Ferrate and Ferric Chloride

The turbidity results indicated that for 23 and 230 mg/l, the lowest values were obtained for the ferrate prepared with calcium and the ferric coagulants; while for the optimum dose, 5000 mg/l, there was only a slight difference between all the products used for the experiments. For this type of sludge the improvement in the dewaterability of the sludge was not seen when calcium was used either with ferrate or with ferric chloride. The results are presented in Figure 4.48.

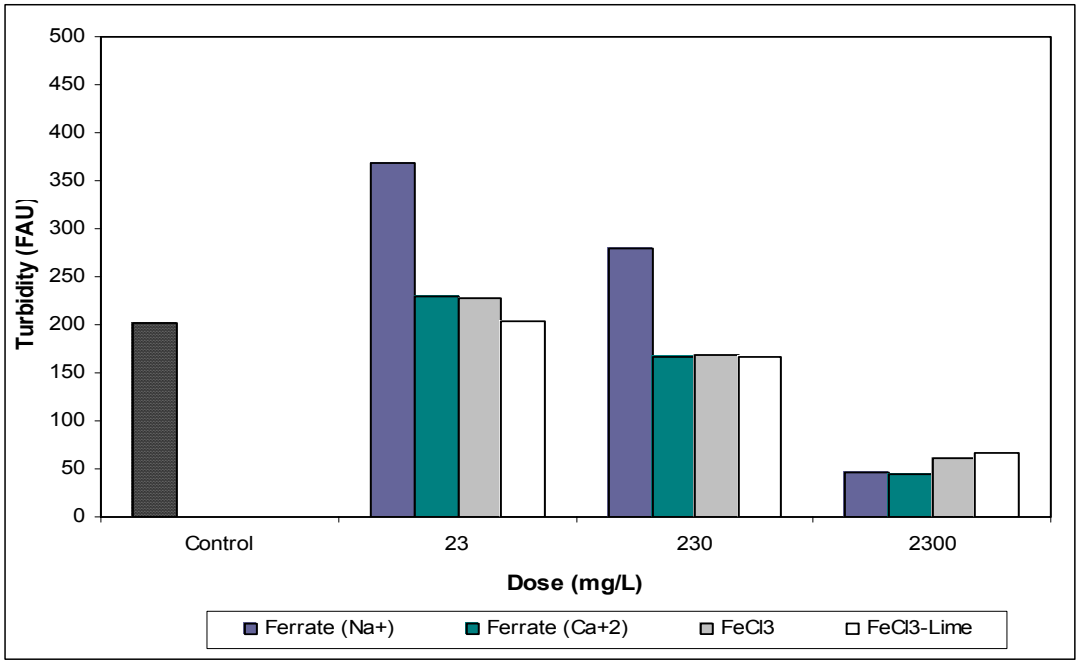


Figure 4.48 Turbidity for the supernatant after centrifugation of Anaerobic Digested Sludge Conditioned Using Different Doses of Ferrate and Ferric Chloride.

From the CST tests it was observed that the lowest CST values were obtained for the maximum dose for all the coagulants used. For the ferrate products, the lowest CST times were observed for the ferrate prepared with sodium at all doses. For the ferric chloride, however, the lowest CST times were observed when ferric was used without lime for 230 and 2300 mg/l, and for ferric with lime for 50 mg/l. Once again it was observed that significant improvement in filtration was not achieved when calcium was added either with ferrate or ferric chloride. The results are shown in Figure 4.49.

The results also indicated that for a dose of 23 mg/l ferrate can be more effective than ferric chloride, while for the optimum dose of 2300 mg/l both conditioners offer the

same results. The results also show that for a dose of 230 mg/l the ferric chloride was more effective than ferrate.

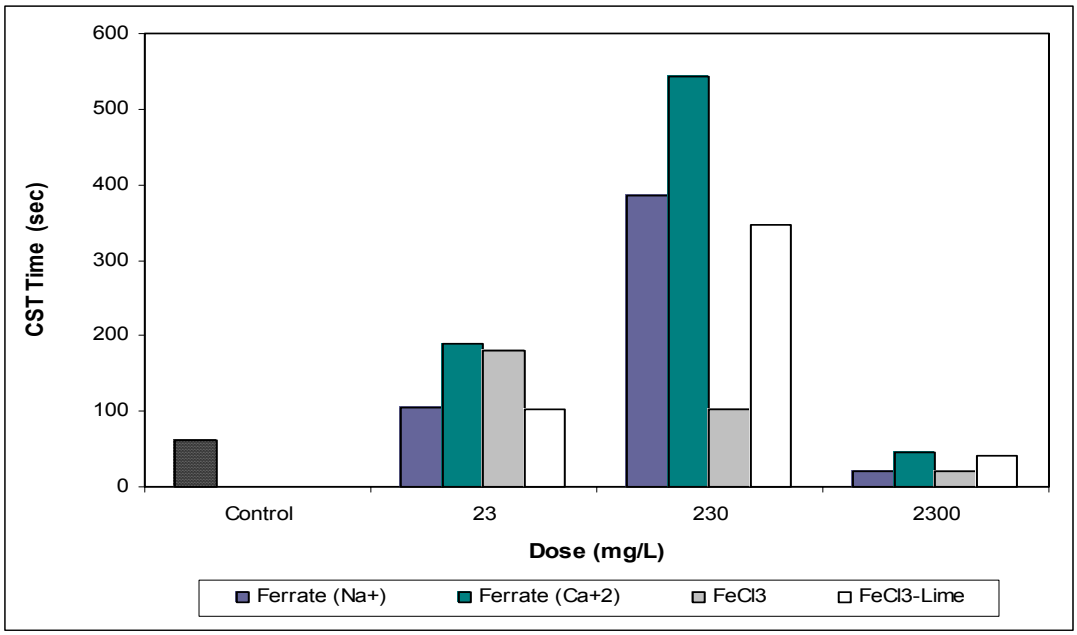


Figure 4.49 CST Times for Anaerobic Digested Sludge Conditioned with Different Doses of Ferrate and Ferric Chloride.

4.2.2.4 Ferrate vs Polymer

The effectiveness of the cationic C-6288 polymer dose of 28 mg/l (currently used at the Southern Water Reclamation) was compared with the optimum ferrate doses at optimum pH for each of the ferrate products used in this study. Both centrifugation and filtration were evaluated.

The centrifugation results indicate that the optimum doses for each of the ferrate products were more effective than the polymer alone, as is shown in Figure 4.50. The volume occupied by solids were 5 ml for the sodium product and 6.25 ml for the calcium product compare to 15 ml for the polymer.

The solid contents were 12% and 10% for the sodium and calcium products, respectively, and 4.2% for the polymer as shown in Figure 4.51. It was also found that the turbidity of the supernatant obtained when both ferrate products were used was lower than the turbidity observed when the polymer dose was used. The turbidity was 77% and 76% of the control for the sodium and calcium products, respectively, compared with 44.8% reduction for the polymer. The results are presented in Figure 4.52.

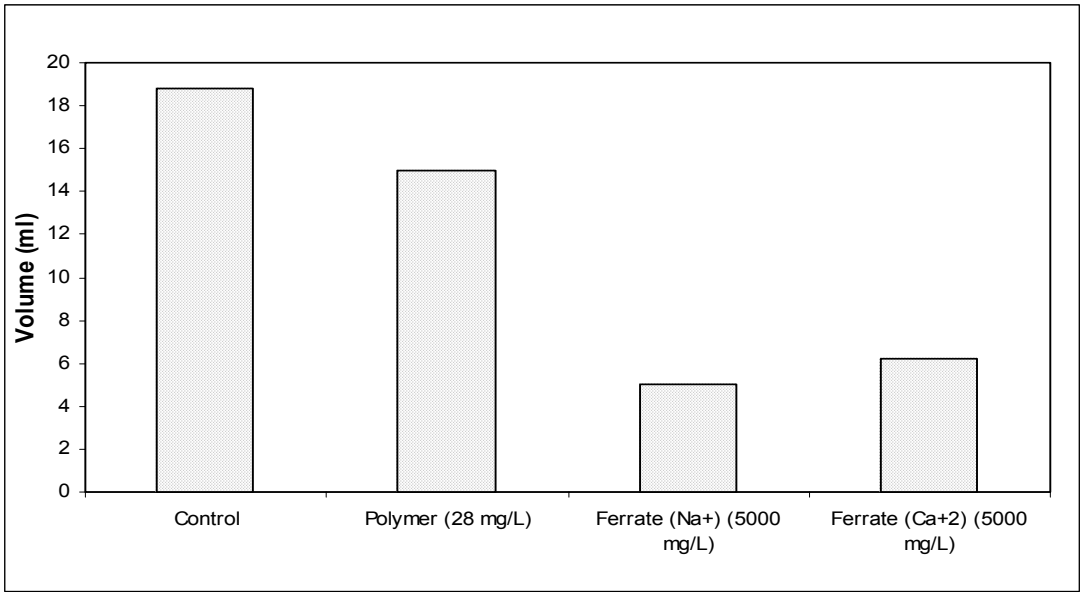


Figure 4.50 Volume Occupied by solids for Anaerobic Digested Sludge Conditioned with Ferrate and Polymer

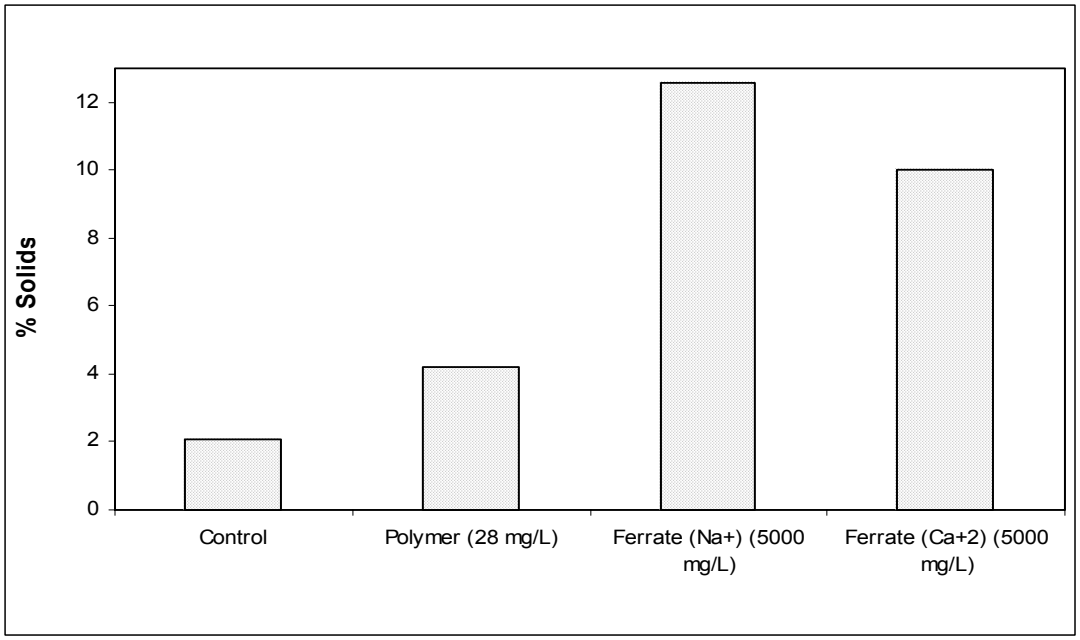


Figure 4.51 Percent Solids on the Cake for Anaerobic Digested Sludge Conditioned with Ferrate and Polymer

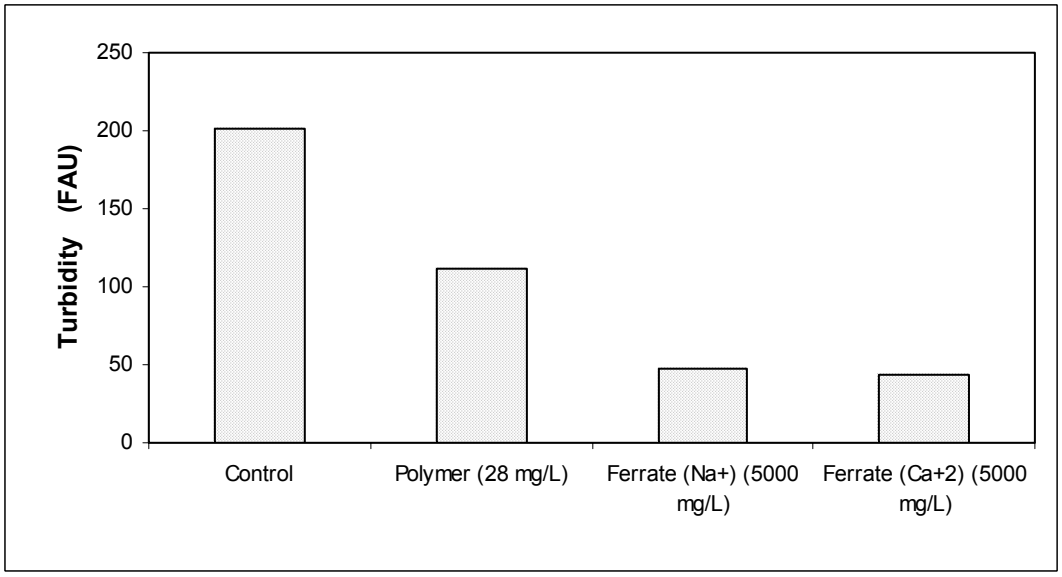


Figure 4.52 Turbidity of the Supernatant after Centrifugation for Anaerobic Digested Sludge Conditioned with Ferrate and Polymer.

The CST results presented in Figure 4.53 indicate that the sodium ferrate was as effective as the polymer dose offering a 67% in the CST for the control (62.6 sec). The reduction attained with the ferrate prepared with calcium was 29%. On the other hand, it was also observed that the calcium ferrate reduced the CST time only by 28% over the control, but the reduction was less than that achieved with the polymer alone.

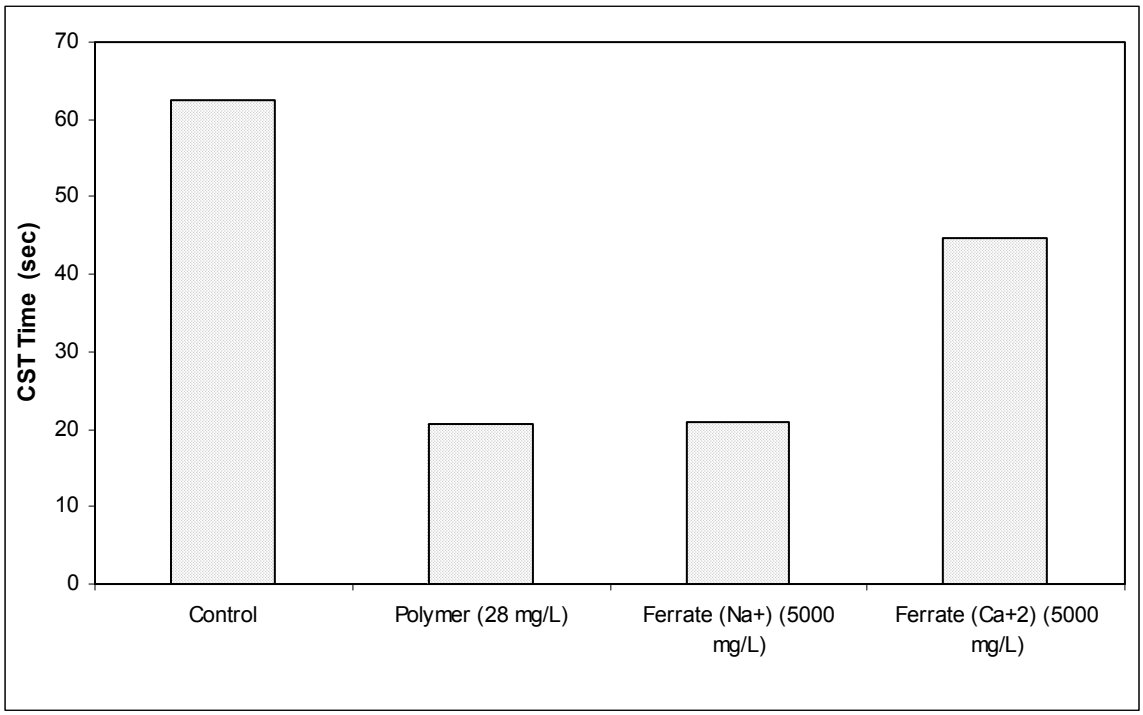


Figure 4.53 CST Times for Anaerobic Digested Sludge Conditioned with Ferrate and Polymer

4.3 Cost Analysis

The cost of using the optimum ferrate dose for the conditioning of waste activated sludge was compared with the actual costs for conditioning chemicals currently used at the Eastern Water Reclamation where the samples were collected. In the same way, the actual cost for the treatment of the sludge to achieve Biosolids Class B was compared with the cost of using the potential ferrate dose for disinfection.

4.3.1 Waste Activated Sludge

For the waste activated sludge, two costs were evaluated. The first cost was that of conditioning using an optimum dose of 10 mg/l of the ferrate (Ca^{+2}) at pH 7.0. This cost was compared with the actual cost of using a dose of 0.05 mg/l of cationic Zetag 7848 polymer. The cost of the acid needed to adjust the pH was considered as well for the calculation of the ferrate cost.

The price of the ferrate product was provided by Ferrate Treatment Technologies, LLC (Orlando, Fl), the polymer price was provided by the Fort Bend Services, Inc.(Stafford , TX), and the price of the hydrochloric acid was provided by UNIVAR.(Jacksonville, Fl). The final costs are presented in Table 4.2.

Table 4.2 Costs of Conditioning for the Waste Activated Sludge

Mechanism of Dewatering	Product	Dose (mg/l)	Cost ($/dry ton)
Centrifugation	Ferrate Prepared with Calcium	10	3.5
	Cationic Zetag 7848 polymer	0.05	7.30
Filtration	Ferrate Prepared with Calcium	10	3.58
	Cationic Zetag 7848 polymer	0.05	7.30

These cost results indicate that the use of ferrate (Ca^{+2}) is cost-effective if it is used for filtration/conditioning and represents a 34.5% reduction in the cost that is currently paid by the wastewater treatment plant in chemicals. The results also indicate that ferrate is cost effective for centrifugation. Furthermore, the solids content on the cake obtained when ferrate is used is 2.2% greater than that obtained when polymer is used.

The second analysis was the cost of using ferrate and polymer together to achieve conditioning and disinfection (Biosolids Class B) in a single dosing and mixing unit process compared with the costs that the plant currently pays for conditioning and disinfection. The cost analysis were performed using a potential ferrate dose of 60 mg/l that allows reducing the fecal coliforms from $4x10^6$ Most Probable Number (MPN) to 18 MPN and meets Class B biosolids regulations (Kim 2004). These are the type of biosolids currently produced by the Eastern Water Reclamation Facility. For the

alternative of using ferrate in combination with polymer to achieve conditioning and disinfection in a single unit process the cost estimated includes; (1) cost of polymer, (2) cost of ferrate, and (3) the transportation cost for the final disposal of the sludge. The current cost paid for the water reclamation facility includes; (1) cost of polymer for conditioning, and (2) the cost paid to the contractors to disinfect and dispose the dewatered sludge. These costs are shown in Table 4.3. The cost did not include the difference in the result mass of sludge cake. However, it has to be recognized that the solids addition due to ferrate is minimal compared to the addition when lime is used. The solids added if ferrate is used based on a 60 mg/l dose would be 0.06lb/lb of sludge compared to 0.4lb/lb of sludge when lime is used. This increase in solids would increase the cost of transportation of the final treated sludge.

Table 4.3 Costs of Conditioning and Disinfection for Waste Activated Sludge when Ferrate and Polymer are Used Together for Class B Biosolids

Mechanism of Dewatering	Product	Ferrate Dose (mg/l)	Polymer Dose (mg/l)	Cost ($/dry ton)
Centrifugation	Ferrate and Polymer	60	0.02	28.0
	Current*		0.05	32.0
Filtration	Ferrate Prepared and Polymer	60	0.02	28.0
	Current		0.05	36.0

* Polymer, Belt filtration, and disposal of sludge.

These results indicate that the use of ferrate and polymer to achieve conditioning and disinfection in a single dose is cost effective compared to the cost that is currently paid by the wastewater treatment plant representing a cost reduction of 12.5%.

If a dose of 119 mg/l would be required for disinfection to achieve biosolids Class A, the cost would be $50/dry ton.

4.3.2 Anaerobic Digested Sludge

For the anaerobic digested sludge, the polymer currently used is more cost effective than the polymer since the dose of ferrate required is much higher than the required dose for polymer, which indicates that the use of ferrate for the dewatering of anaerobic digested sludge is not cost effective.

5 CONCLUSIONS AND RECOMENDATIONS

The main objective of this research was to evaluate the effectiveness of ferrate in dewatering of biosolids. During this research experiments were conducted to quantify the possible volume reduction of the sludge and the filtration time after conditioning with ferrate using centrifugation and the Capillary Suction Time test, respectively. Samples of anaerobic digested sludge from the Southern Water Reclamation Facility (Orlando, Fl) and waste activated sludge form the Eastern Water Reclamation Facility (Orlando, Fl) were used for conditioning with ferrate. Two different ferrate products, one prepared with calcium hypochlorite and another one prepared with sodium hypochlorite were used in this study.

The optimum conditions for pH, rotational speed and time to achieve mechanical equilibrium were defined for each type of sludge conditioned with ferrate, and the optimum dose for each ferrate product was determined under those conditions. Comparisons between the effectiveness of the ferrate product with that for polymer doses currently used at the wastewater treatment plant where the samples were collected, and ferric coagulants were made.

Additional experiments were conducted to evaluate the alternative of using ferrate and polymer together to achieve dewatering and disinfection in a single dosing and mixing unit process, and to reduce the polymer dose and cost for sludge treatment.

Finally, a cost analysis was done calculating the cost of using the optimum ferrate doses to condition each type of sludge and comparing those costs with the actual costs for conditioning chemicals currently used in the wastewater treatment plants where the samples were collected. Based on the results of this research, the following conclusions can be drawn:

- The optimum conditions for the dewatering of anaerobic digested sludge conditioned with ferrate are pH 7, rotational speed of 2400 rpm, and a time of 1800 seconds to achieve mechanical equilibrium. The same conditions for the waste activated sludge are pH 7, rotational speed of 800 rpm, and 1800 seconds.
- The optimum dose of ferrate for the conditioning of waste activated sludge at pH 7 is 10 mg/l for filtration and centrifugation.
- Ferrate added for the conditioning of activated sludge is a more effective conditioner that the ferric iron when directly added.
- The addition of calcium during the conditioning of waste activated sludge enhances the dewaterability of the sludge. Thus, the ferrate (Ca^{+2}) is a more suitable product for conditioning and provides higher volume reduction during filtration and lower times of filtration that those obtained for the ferrate (Na^{+}).
- When dewatered biosolids are used in land applications for agricultural purposes the used of ferrate (Na^{+}) may have adverse effects because the amounts of sodium and sodium chloride present on the ferrate may reduce the water uptake by plant roots due to the high osmotic potential that is generated.

- Ferrate is a cost-effective conditioner for the conditioning of activated sludge when filtration or centrifugations are used as mechanical aid. It provides a 8.3% reduction in the filtration time, a 40% in the volume occupied by solids, and 51% reduction in the cost for conditioning.
- The use of ferrate and polymer for the conditioning and disinfection of the waste activated sludge was a cost-effective alternative which could reduce the actual cost by 12.5%.
- Ferrate is an effective conditioner for anaerobic digested sludge when filtration and centrifugation were used as mechanical aids for dewatering. The optimum dose on both cases was 5000 mg/l.
- For the anaerobic digested sludge the addition of calcium does not offer an improvement for the conditioning of the sludge since significant improvement was not observed when the calcium ferrate was compared with the sodium ferrate.
- The optimum ferrate dose for the conditioning of anaerobic digested sludge provides the same time to filtration than that for the polymer, and during centrifugation provided higher volume reduction and percent solids improvement for the cake than polymer. However is not cost-effective when because a much higher dose than that used for polymer has to be used.

Based on the results of this research, the following recommendations are made for future laboratory and field research:

- Pilot studies for the conditioning of the waste activated sludge using the optimum dose of 10 mg/l of ferrate are recommended to evaluate the future implementation of ferrate when devices such us belt filter presses based on filtration are used for dewatering operations.
- The optimum dose of the calcium ferrate for the conditioning of waste activated sludge should be evaluated given than less ferrate may be needed to achieve similar results to those obtained for the sodium ferrate product.
- The estimated dose for disinfection of the sludge required to achieve biosolids Class B has to be evaluated given that less ferrate may be needed to achieve the $2x10^6$ MPN for fecal coliform required by the CFR 40 part 503 for biosolids. The current dose of 60 mg/l reduces the fecal coliform to 18 MPN. A reduction in dose will lower the cost.
- Quantification of the impact of the amounts of the sodium and sodium chloride present in the sodium ferrate added to biosolids on soil water availability to plants is recommended when the dewatered biosolids are used for agricultural purposes.

While effective in conditioning waste activated sludge, ferrate can also disinfect the sludge. Therefore, more experimental studies should be dedicated to determine the minimum dose required for disinfection of the sludge, and the possibility of achieving

conditioning and disinfection in one single dose. Ferrate is a promising product that can be used as a viable alternative to reduce the cost of these operations and eliminate the need for the addition of two chemicals, to achieve dewatering and disinfection..

APPENDIX A

RAW DATA FOR INITIAL EXPERIMENTS

Figures A1 and Figure A2 show the results obtained for initial experiments for the conditioning of waste activated sludge and anaerobic digested sludge using sodium ferrate. These results were obtained from centrifugation trials for which a wide range of ferrate doses and the volume occupied by solids for each dose were evaluated.

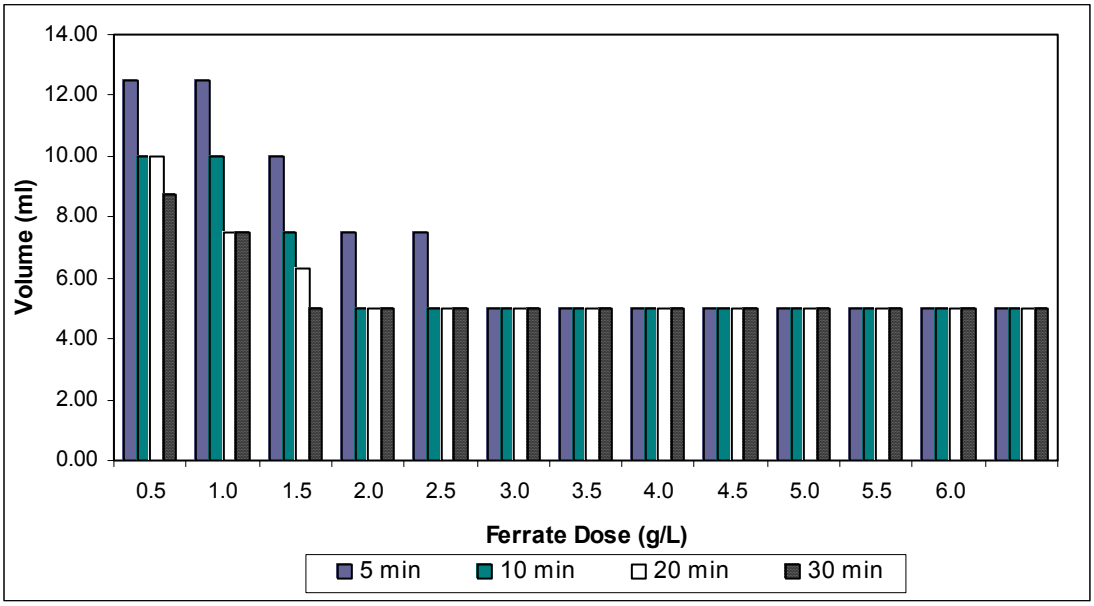


Figure A1 Volume Occupied by Solids for Waste Activated Sludge Conditioned with Sodium Ferrate after Centrifugation.

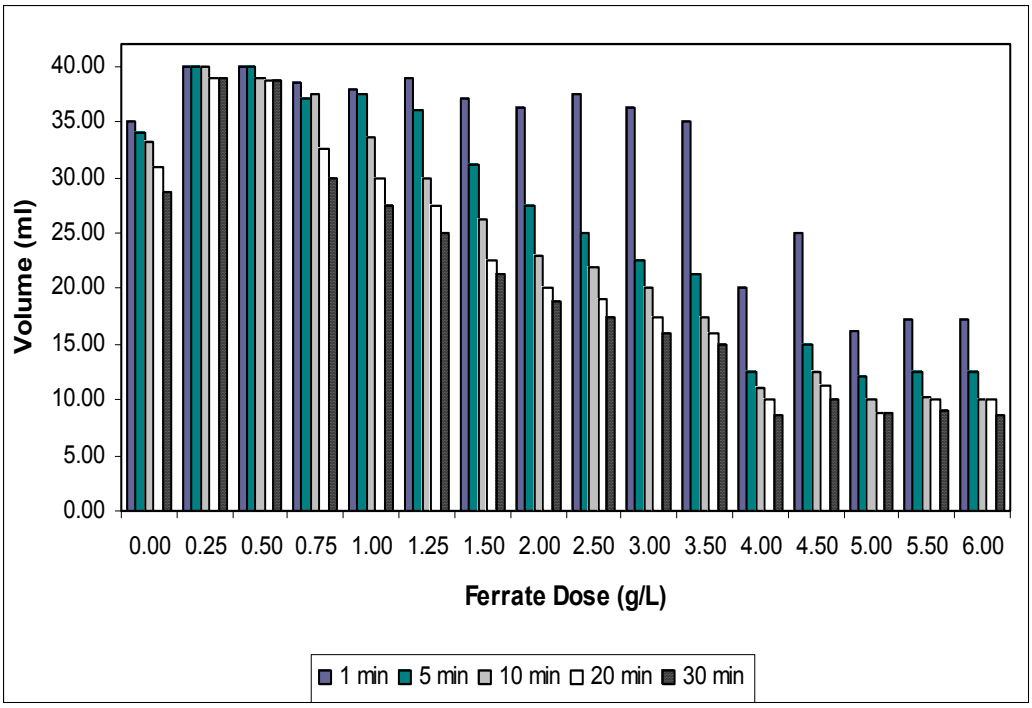


Figure A2 Volume Occupied by Solids for Anaerobic Digested Sludge Conditioned with Sodium Ferrate after Centrifugation

APPENDIX B

REGULATIONS FOR PATHOGENS IN BIOSOLIDS

Table C1 Maximum Concentrations of Pathogens Permitted in Biosolids

Species	Biosolids Class
	Class A
Salmonella sp.	Less than 3 MPN per 4 g total solids (or less than 1x 10^3 MPN fecal coliforms per gram total solids)
Enteric Viruses	Less than 1 MPN per 4 g total solids
Viable Ova	Less than 1 MPN per 4 g total solids
	Class B
Fecal coliforms	Less than 2 x 10^6 colony –forming units (CFUs) per gram total solids

APPENDIX C

RAW DATA FOR EXPERIMENTS

Waste Activated Sludge

Table C1 Optimum Dose for Ferrate (Na+)

Dose (mg/l)	Centrifugation	Filtration
	Volume Occupied by solids (ml)	CST Time (sec)
Control	12.5	22.7
Polymer	11.2	10.5
1	15.0	24.0
2	15.0	20.5
4	15.0	21.6
6	15.0	22.6
8	7.50	28.7
10	7.50	13.2
20	7.50	14.1
40	8.75	52.9
60	7.50	100.0
80	8.75	116.5
100	12.5	173.3
120	10.0	169.0
140	10.0	193.6
160	10.0	235.7
180	10.0	143.3
200	9.00	147.4
400	10.	127.4
600	8.75	136.2
800	7.50	175.6
1000	6.50	165.8

Table C2. Calcium vs. Sodium (Centrifugation)

Ferrate Product	Dose (mg/l)	Volume Occupied by solids (ml)				
		Time (min)				
		1	5	10	20	30
		(ml)	(ml)	(ml)	(ml)	(ml)
None	Control	35.00	18.75	15.00	12.50	12.50
None	Polymer	17.50	12.50	12.50	11.25	10.00
Ferrate (Ca^{+2})	10	20.00	12.50	11.25	7.50	7.50
	100	12.50	10.00	10.00	7.50	7.50
	1000	10.00	7.50	7.50	6.50	6.25
Ferrate (Na^{+})	10	20.00	12.50	10.00	8.75	7.50
	100	20.00	17.50	15.00	13.75	12.50
	1000	12.50	10.00	9.00	8.75	7.50

Table C3. Calcium vs. Sodium (CST Times)

Time	Control	Polymer	Calcium (sec)			Sodium (sec)		
			10 mg/l	100 mg/l	1000 mg/l	10 mg/l	100 mg/l	1000 mg/l
1	25.0	10.1	8.7	77.6	21.7	12.8	172.8	165.1
2	18.0	9.8	9.1	86.7	21.9	14.0	180.3	166.2
3	25.6	11.7	8.5	83.8	21.3	13.1	175.1	165.8
4	23.8	9.5	9.0	78.9	20.9	12.8	168.2	165.0
5	21.0	11.6	8.6	76.0	21.7	13.2	170.1	166.9
Average.	22.7	10.5	8.8	80.6	21.5	13.2	173.3	165.8
Stdv	3.16	1.04	0.26	4.49	0.40	0.49	4.71	0.79

Table C4. Ferric Chloride and Ferric Chloride and Lime (Centrifugation)

Coagulant	Dose (mg/l)	Volume Occupied by Solids (ml)					
		Time (min)					
		1	5	10	20	30	40
		(ml)	(ml)	(ml)	(ml)	(ml)	(ml)
Ferric alone	4.7	20.00	12.50	10.00	8.75	7.50	7.50
	47	12.50	10.00	10.00	7.50	7.50	7.50
	470	10.00	7.50	7.50	6.50	6.25	6.00
Ferric and Lime	4.7	32.50	20.00	15.00	12.50	11.20	11.00
	47	36.25	22.50	17.50	15.00	12.50	12.50
	470	28.75	16.00	14.00	13.70	13.70	13.70

Table C5. Ferric Chloride and Ferric Chloride and Lime (CST Times)

Time	Ferric + Lime			Ferric		
	4.7 mg/l	47 mg/l	470 mg/l	4.7 mg/l	47 mg/l	470 mg/l
1	14.2	11.7	10.9	20.8	18.5	9.6
2	12.9	12.0	10.0	22.6	18.9	9.8
3	12.5	11.9	11.3	21.8	18.5	8.9
4	12.9	11.8	10.7	22.6	18.2	8.5
5	14.1	11.9	10.3	20.9	17.9	9.0
Average	13.3	11.9	10.6	21.7	18.4	9.2
Stdv	0.78	0.11	0.51	0.88	0.37	0.53

Table C6. Ferrate (Na^+) and Polymer at pH 7.0 (Centrifugation)

Polymer dose (mg/l)	Volume Occupied by solids (ml)				
	Time (min)				
	1	5	10	20	30
	(ml)	(ml)	(ml)	(ml)	(ml)
0	35.00	18.75	15.00	12.50	12.50
0.05	13.75	12.50	11.25	11.25	11.25
0.008	9.00	8.25	8.00	7.75	7.75
0.002	6.25	5.00	4.75	4.75	5.00
0.025	9.00	6.25	6.25	6.25	6.25
0.033	8.75	7.50	6.25	6.25	6.25
0.042	8.75	7.50	7.00	6.25	6.25
0.050	11.25	10.00	8.75	8.75	7.50

Table C7. Ferrate (Na^+) and Polymer with no pH Adjustment (Centrifugation)

Polymer Dose (mg/l)	Volume Occupied by Solids (ml)				
	Time (min)				
	1	5	10	20	30
	(ml)	(ml)	(ml)	(ml)	(ml)
0	35.00	18.75	15.00	12.50	12.50
0.05	13.75	12.50	11.25	11.25	11.25
0.008	25.00	22.50	17.50	15.00	15.00
0.002	32.50	27.50	25.00	25.00	25.00
0.025	27.50	22.50	20.00	18.75	18.75
0.033	30.00	27.50	27.50	25.00	25.00
0.042	25.00	17.50	15.00	12.50	12.50
0.050	30.00	27.50	26.26	25.00	22.50

Table C8. Ferrate (Ca^{+2}) and Polymer at pH 7.0

Polymer Dose (mg/l)	Volume Occupied by Solids					
	Time (min)					
	1	5	10	20	30	40
	(ml)	(ml)	(ml)	(ml)	(ml)	(ml)
0	35.00	18.75	15.00	12.50	12.50	12.50
0.05	13.75	12.50	11.25	11.25	11.25	11.25
0.008	17.50	16.25	12.50	10.00	8.25	8.25
0.002	13.25	12.50	8.75	7.50	7.50	7.50
0.025	17.50	12.50	10.00	10.00	10.00	10.00
0.033	12.50	11.25	10.00	10.00	10.00	10.00
0.042	15.00	11.25	10.00	10.00	10.00	10.00
0.050	15.00	11.25	10.00	8.75	8.75	8.75

Table C9. Ferrate (Ca^{+2}) and Polymer with no pH adjustment

Polymer Dose (mg/l)	Volume Occupied by Solids				
	Time (min)				
	1	5	10	20	30
	(ml)	(ml)	(ml)	(ml)	(ml)
0	35.00	18.75	15.00	12.50	12.50
0.05	13.75	12.50	11.25	11.25	11.25
0.008	15.00	8.75	7.50	6.25	6.00
0.002	13.25	8.25	7.50	5.00	5.00
0.025	11.25	10.00	8.25	7.50	6.25
0.033	11.00	7.50	6.25	5.00	5.00
0.042	15.00	13.75	10.00	8.75	8.75
0.050	17.50	12.50	10.00	10.00	10.00

Table C9. Ferrate (Na^{+}) and Polymer at pH 7.0 (CST Times)

Time	Control	Polymer (0.05 mg/l)	Polymer Doses (mg/l)					
			0.008	0.020	0.025	0.033	0.042	0.050
			(sec)	(sec)	(sec)	(sec)	(sec)	(sec)
1	21.7	10.1	90.0	58.5	63.5	98.9	161.0	225.8
2	20.7	9.8	88.9	57.0	62.5	102.5	168.9	215.9
3	19.8	11.7	86.0	56.5	63.8	101.3	159.8	221.6
4	20.7	9.5	88.9	59.0	64.5	100.8	160.1	228.6
5	19.1	11.6	87.9	52.3	66.8	101.5	153.2	227.2
Average	20.4	10.5	88.3	55.8	64.2	101.0	152.1	223.8
Stdv	0.99	1.04	1.50	2.65	1.61	1.33	5.58	5.14

Table C10. Ferrate (Na^{+}) and Polymer with no pH Adjustment (CST Times)

Time	Control	Polymer (0.05 mg/l)	Polymer Dose (mg/l)					
			0.008	0.002	0.025	0.033	0.042	0.050
			(sec)	(sec)	(sec)	(sec)	(sec)	(sec)
1	21.7	10.1	465.3	415.8	430.8	585.6	552.3	589.2
2	20.7	9.8	463.2	435.9	439.5	584.2	553.2	585.8
3	19.8	11.7	469.2	432.6	436.9	583.2	557.8	571.2
4	20.7	9.5	475.2	425.6	437.8	587.6	548.3	583.5
5	19.1	11.6	460.2	426.8	450.0	575.2	551.3	589
Average	20.4	10.5	466.6	427.3	439.0	583.2	552.6	583.8
Stdv	0.99	1.04	5.81	7.70	6.97	4.75	3.45	7.40

Table C11. Ferrate (Ca^{+2}) and Polymer at pH 7.0 (CST Times)

Time	Control	Polymer (0.05 mg/l)	Polymer Dose (mg/l)					
			0.008	0.002	0.025	0.033	0.042	0.050
			(sec)	(sec)	(sec)	(sec)	(sec)	(sec)
1	21.7	10.1	44.1	23.2	35.3	69.8	77.9	95.3
2	20.7	9.8	45.6	22.5	38.9	67.5	78.9	98.6
3	19.8	11.7	43.8	25.3	34.9	69.6	76.5	92.4
4	20.7	9.5	46.8	22.8	37.6	65.3	79.1	93.5
5	19.1	11.6	45.1	23.1	35.0	65.8	78.5	96.7
Average	20.4	10.5	45.1	23.4	36.3	67.6	78.2	98.1
Stdv	0.99	1.04	1.21	1.11	1.81	2.08	1.04	2.47

Table C12. Ferrate (Ca^{+2}) and Polymer with no pH Adjustment (CST Times)

Time	Control	Polymer (0.05 mg/l)	Polymer Dose (mg/l)					
			0.008	0.002	0.025	0.033	0.042	0.050
			(sec)	(sec)	(sec)	(sec)	(sec)	(sec)
1	21.7	10.1	115.8	150.3	198.5	238.1	215.6	250.8
2	20.7	9.8	116.9	156.3	199.2	226.8	208.6	253.6
3	19.8	11.7	114.2	158.6	197.6	229.5	209.3	258.9
4	20.7	9.5	115.6	153.2	201.5	230.1	215.3	259.3
5	19.1	11.6	115.8	158.9	199.5	232.2	216.8	262.3
Average			115.7	155.5	199.3	231.3	213.1	257.0
Stdv	0.99	1.04	0.96	3.68	1.45	4.24	3.86	4.66

Anaerobic Digested Sludge

Table C13. Optimum Dose for Ferrate (Na+)

Dose (mg/l)	Centrifugation	Filtration
	Volume Occupied by Solids (ml)	CST Time (sec)
Control	18.75	62.6
10.12	18.75	160.0
20	18.75	123.0
40	18.75	105.0
60	17.50	115.2
80	18.75	102.8
100	18.75	**202.8**
200	17.50	221.0
300	17.00	210.1
400	15.00	206.1
500	17.50	116.5
1000	15.00	386.7
1500	12.50	545.4
2000	10.00	400.5
2500	7.50	292.1
3000	6.25	175.4
3500	6.25	159.9
4000	7.50	101.2
4500	6.00	85.0
5000	5.00	55.0
5500	5.00	52.0
6000	5.00	61.0

Table C14. Calcium vs. Sodium (Centrifugation)

Ferrate	Dose (mg/l)	Volume Occupied by Solids				
		Time (min)				
		1	5	10	20	30
		(ml)	(ml)	(ml)	(ml)	(ml)
None	Control	35.00	22.50	20.00	17.50	18.75
None	Polymer	31.25	21.25	19.00	17.50	16.25
Ferrate (Ca^{+2})	50	35.00	22.50	20.00	18.75	18.75
	500	28.25	23.25	21.25	20.00	18.75
	5000	11.25	7.50	7.50	6.50	6.25
Ferrate (Na^{+})	50	35.00	22.50	20.00	17.50	18.75
	500	26.25	20.00	20.00	17.50	17.50
	5000	7.50	6.20	6.25	6.10	5.00

Table C15. Calcium vs. Sodium (CST Time)

Time	Control	Polymer	Calcium			Sodium		
			50 mg/l	500 mg/l	5000 mg/l	50 mg/l	500 mg/l	5000 mg/l
1	60.8	22.8	185.9	541.2	43.9	105.4	388.9	20.5
2	62.5	21.5	196.8	550.2	45.7	103.4	390.1	20.6
3	63.4	19.5	190.0	548.2	46.5	108.3	385.1	21.5
4	60.5	21.8	191.0	537.5	43.1	107.5	388.9	20.8
5	65.9	17.5	187.9	539.9	43.9	103.2	380.1	20.8
Average.	62.6	20.6	190.3	543.4	44.6	105.6	386.6	20.8
Stdv	2.19	1.04	4.12	5.50	1.42	2.32	4.10	0.39

Table C16. Ferric Chloride vs. Ferric Chloride and Lime (Centrifugation)

Coagulant	Volume Occupied by Solids					
		Time (min)				
	Dose	1	5	10	20	30
	(g/L)	(ml)	(ml)	(ml)	(ml)	(ml)
	Control	35.00	22.50	20.00	17.50	18.75
	Polymer	31.25	21.25	19.00	17.50	16.25
Ferric Alone	23	35.00	22.50	20.00	18.75	18.75
	230	28.25	23.25	21.25	20.00	18.75
	2300	25.00	17.50	16.25	15.00	15.00
Ferric with Lime	23	35.00	25.00	21.25	20.00	18.75
	230	32.50	22.50	20.00	17.50	17.50
	2300	25.00	17.50	16.25	15.00	15.00

Table C16. Ferric Chloride vs. Ferric Chloride and Lime (CST Times)

Time	Control	Polymer	Ferric + Lime			Ferric		
			23 mg/l	230 mg/l	2300 mg/l	23 mg/l	230 mg/l	2300 mg/l
1	60.8	22.8	100.0	348.9	42.2	178.9	103.5	20.5
2	62.5	21.5	102.3	346.8	38.9	179.5	101.4	20.9
3	63.4	19.5	103.5	347.5	35.0	179.8	102.8	21.2
4	60.5	21.8	102.8	348.0	43.5	180.1	100.9	20.5
5	65.9	17.5	100.1	338.9	42.6	180.2	101.2	21.1
Average.	62.6	20.6	101.7	346.0	40.4	179.7	102.0	20.8
Stdv	2.19	2.12	1.60	4.05	3.50	0.52	1.13	0.33

LIST OF REFERENCES

Albertson, O.E. (1991). Dewatering municipal wastewater sludges. New Jersey: Noyes Data Corp.

Basu, A., Williams, K., and Modak, M.J. (1987). Ferrate oxidation of Escherichia coli DNA Polymerase-I. The Journal of Biological Chemistry 262(20), 9601-9607.

Bielski, B.H. and Thomas, M.J. (1987). Studies of hypervalent iron in aqueous solutions. Radiation indiced reduction of iron (VI) to iron (V) by CO_2^-. Journal of American Chemical Society 109, 7761-7764.

Chu, C.P. and Lee, D.J. (2000). Experimental analysis of centrifugal dewatering process of polyelectrolyte flocculated waste activated sludge. Water Research 35(10), 2377-2384.

Colin, F. and Gazbar, S. (1995). Distribution of water in sludges in relation to their mechanical dewatering. Water Research 29(8), 2000-2005.

De Luca, S., Idle, C.N., and Chao, A.C. (1996). Quality improvement f biosolids by ferrate (VI) oxidation of offensive odor compounds. *Water Science and Technology* 33(3), 119-130.

De Luca, S., Cantelli, M., and DeLuca, M.A. (1992). Ferrate vs traditional coagulants in the treatment of combined industrial wastes. Water Science and Technology 23, 9-11.

Gilbert, M. Waite, T.D., and Hare, C. (1976). Applications of ferrate ion to disinfection. Journal of American Water Works Association 56, 466-474.

Goff, H. and Murman, R.K. (1971). Studies on the mechanism of isotopic oxidation and reduction of ferrate (VI) ion (FeO_4^{-2}). Journal of American Chemical Society 93(23), 6058-6065.

Guan, J. Amal, R., and Waite, T.D. (2003). Effect of floc size and structure on biosolids capillary suction time. Water Science and Technology 47(12), 255-260.

Gujar, B.R. (2001). Sludge Treatment and disposal. A.A. Balkema.

Houghton, J.I. and Stephenson, T. (2002). Effect of influent content on digested sludge extracellular polymer content and dewaterability. Water Research 36(14), 3620-3628.

Katsiris, N. and Kouzeli-Katsiri, A. (1987). Bound water content of biological sludges in relation to filtration and dewatering. Water Research 21(116), 1319-1327.

Kazama, F. (1995). Viral inactivation by potassium ferrate. Water Science and Technology 31, 165-168.

Kim, H. (2004). Testing of Innovative Ferrate Technology for Sludge Management. University of Maryland. Washingotn D.C.

Hogg, R. (2000). Flocculation and Dewatering. International Journal of Mineral Processing. 58, 223-236.

Lamsal, K., Paudyal, G.N., and Saeed M. (1999). Model for assessing impact of salinity on soil water availability and crop yield. Agricultural Water Management 41, 57-70.

Langer, S.J., Klute, R., and Hahn, H.H. (1994). Mechanisms of floc formation in sludge conditioning with polymers. Water Science and Technology 30(8), 129-138.

Lee, S.J., Chu, C.P., Tan, B.H., Wang, C.H., and Lee, D.J. (2003). Consolidation dewatering and centrifugal sedimentation of flocculated activated sludge. Chemical Engineering Science 58(9), 1687-1701.

Lee,Y.,. Cho, M., Kim, J.Y., and Yoon, J. (2003). Chemistry of ferrate (Fe(VI)) in aqueous solutions and its applications as a green chemical. J. Industrial Engineering Chemistry 10(1), 161-171.

Liao, B.Q., Allen, D.G., Droppo, I.G., Leppard, G.G., and Liss, S.N. (2001). Surface properties of sludge and their role in bioflocculation and settleability. Water Research 35(2), 339-350.

Ma, J. and Liu, W. (2002). Effectiveness of ferrate (VI) preoxidation in enhancing the couagulation of surface waters. Water Research 36(20), 4959-4962.

McFarland, M.J. (2000). Biosolids engineering. New York: Mc Graw-Hill.

Mikkelsen, L.H. and Keiding, K. (2002). Physico-chemical characteristics of full scale sewage sludges with implications to dewatering. Water Research 36, 2451-2462.

Neyens, E., Baeyens, J., Dewil, R., and Deheyder, B. (2004). Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering. Journal of Hazardous Materials 106B, 83-92.

Nellenshulte, T., and Kayser, R. (1997). Change in particle structure of sewage sludges during ,mechanical and biological processes with regard to the dewatering result. Water Science and Technology 36(4), 293-306.

Norcross,B.E., Lewis, W.C., Gain, H., Noureldin, N.A, and Lee, D.G. (1997) Canadian Journal of Chemistry.75, 129-136.

Novak, J.T., Agerbaek, M.L., Sorensen, B.L., and Hansen, J.A. (1999). Conditioning, Filtering, and Expressing waste activated sludge. Journal of Environmental Engineering 125(9), 816-824.

Novak, T.J. and Higgins, M.J. (1997). Dewatering and settling of activated sludge: The case for using cation analysis. Water Environment Research 69(2), 225-231.

Novak, J.T., Sadler, M.E., and Murthy, S.N. (2003). Mechanism of floc destruction during anaerobic and aerobic digestion and the effect on conditioning and dewatering of biosolids. Water Research 37(13), 3136-3144.

Rush, J.D. and Bielski, B.J. (1989). Kinetics of ferrate (V) decay in neutral and acidic solutions. A pulse radiolysis study. *Inorganic Chemistry* 28, 3947-3951.

Sanin, D.F. and Vesilind, P.A. (1994). Effect of centrifugation on the removal of extracellular polymers and physical properties of activated sludge. Water Science and Technology 30(8), 117-127.

Schreyer, J.M., Ockerman, L.T. (1952). Stability of the ferrate (VI) ion in aqueous solution. Analytical Chemistry. 23 (9)1312_1314.

Schink, T. and Waite, T.D. (1980). Inactivation of f2 virus with ferrate (VI). Water Research 14, 1705-1717.

Sharma, V.K. (2002). Potassium ferrate (VI): an environmental friendly oxidant. Advances in Environmental Research 6(2), 143-156.

Sharma, V.K. (2004). Use of iron (VI) and iron (V) in water and wastewater treatment. Water Science and Technology 49(4), 69-74.

Shien, J. (1988). Sludge Conditioning. Alexandria, VA : Water Pollution Control Federation.

Spellman, F.R. (1997). Dewatering biosolids. Lancaster: Technomic Publications. Standard Methods for the Examination of Water and Wastewater , (20th Edition). 1998.

Eaton, A.D., Greenberg, A.E, and Clesceri, L.S. Published jointly by American Public Health Association, American Water Works Association, and Water Environment Federation: Washington, D.C.

Thompson, M., Ockerman, L.T., and Schreyer, J.M. (1951). Preparation and purification of potassium ferrate (VI). American Chemical Society 73, 1379-1381.

Tixier, N., Guibaud,G., and Baudu,M. (2003). Effect of pH and ionic environment changes on interparticle interactions affecting activated sludge flocs: a reological approach. Environmental Technology 24, 971-978.

U.S. EPA (1993), Domestic Septage Regulatory Guidance: A guide to the EPA 503 Rule. EPA/832/B92/005.

U.S. EPA (1999), Environmental Regulations and Technology-Control of pathogens and vector attraction in sewage sludge. EPA/625/R-92/013, Office of Research and Development Washington, DC 20460.

Vaxelaire, J. and Cezac, P. (2004). Moisture distribution in activated sludges; a review. Water Research 38(9), 2215-2230.

Vesilind, P.A. (1979). Treatment and disposal of wastewater sludges. Michigan :Ann Arbor Sciences.

Vesilind, P.A. and Hsu, C. (1997). Limits of sludge dewaterability. Water Science and Technology 36(11), 87-91.

Vesilind, P.A. and Martel, C.J. (1989). Freezing of water and wastewater sludges. Journal of the Environmental Engineering ASCE, 116, 854-861.

Vaxelaire, J. and Cezac, P. (2004). Moisture distribution in activated sludges: a review. Water Research 38(9), 2215-2230.

Wagner, W.F., Gump, J.R., and Hart, E.N. (1952). Factor affecting the stability of aqueous potassium ferrate (VI) solutions. Analytical Chemistry 24(12), 1947-1948.

Waite, T.D., Fagan, J. (1980). In: Carvey, J. Ed. , Condenser Biofouling Control, Chapter 30. Ann Arbor Science, MI.

White, D.A., and Franklin, G.S. (1998). A preliminary investigation into the use of sodium ferrate in water treatment. Environmental Technology 9, 1157-1160.